RUBBER CHEMISTRY

AND TECHNOLOGY

PEPTON® 22—A Non-Staining Catalytic Plasticizer For SBR and Natural Rubber

A great many chemicals, as well as a number of mechanical treatments, have been tried and used in obtaining or approaching the desired plasticity in natural rubber and synthetic rubber compounds. Many of the chemicals have been objectionable from an odor and toxicity standpoint while the mechanical treatments have been generally slow and power-consuming. A chemical which is not objectionable and which is a highly effective catalytic plasticizer for natural rubber and the various types of SBR is Cyanamid's Pepton 22 Plasticizer.

Pepton 22 Plasticizer is non-staining and will not discolor white or light-colored stocks. It produces good physical properties and has no adverse effect on aging. Pepton 22 Plasticizer can reduce breakdown time by as much as 50%. Power cost reduction and more effective utilization of Banbury and mill mixing equipment can be obtained by using this catalytic plasticizer. Easier mastication with Pepton 22 Plasticizer results in a lower heat history and reduces scorch possibilities. It also results in better control of gel build-up and the Mooney Viscosity shows no appreciable change on standing.

The outstanding activity of Pepton 22 Plasticizer in rubber compounding is illustrated in Cyanamid Technical Bulletin No. 816. Ask your Cyanamid Rubber Chemicals representative for a copy of this informative publication, or write to American Cyanamid Company, Rubber Chemicals Department, Bound Brook, New Jersey.

Guanidines DPG and DOTG As Secondary Accelerators and Activators

The guanidines DPG and DOTG were extensively used as primary accelerators until the early 1930's, when they were largely replaced in that capacity by thiazoles.

As a result of their basicity, however, it was found that the guanidines had a strong activating effect on the thiazoles. Almost before the old application was dead, a new one had opened up for them as secondary accelerators and activators with the various thiazoles and thiazole derivatives, particularly in butadiene-styrene copolymers, which cure at a slower rate than natural rubber. Although they are still sometimes used as primary accelerators in highly loaded mechanical stocks, it is in the capacity of secondary accelerators that guanidines DPG and DOTG find their greatest application today. For example, delayed-action type accelerators, at times, are too slow curing for a particular set of processing conditions. In such cases, the use of DPG or DOTG as secondary accelerators results in a faster curing rate with improved physical properties during the early stages of cure.

The guanidines are proving particularly valuable in stocks for footwear, heels, soles, tires, hard rubber and molded goods in general.

Full details of guanidine accelerators DPG and DOTG are contained in Cyanamid Technical Bulletin No. 848. Ask your Cyanamid Rubber Chemicals representative for your copy, or write to American Cyanamid Company, Rubber Chemicals Department, Bound Brook, New Jersey.

The Division has need of two copies
of RUBBER CHEMISTRY AND
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an excellent state of preservation.
Anyone having an issue available
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Division of Rubber Chemistry, A.C.S.

318 Water Street

Akron 8, Ohio

RUBBER CHEMISTRY

AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY

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FUTURE MEETINGS

Meeting		City	Hotel	Date
1958	Spring	Cincinnati	Netherlands Plaza	May 14–16
1958	Fall	Chicago	Sherman	September 10–12
1959	Spring	Los Angeles	Biltmore	May 12–15
1959	Fall	Washington*	Shoreham	November 9–13
1960	Spring	Buffalo	Statler	May 24–27
1960	Fall	New York	Commodore	September 13–16
1961	Spring	Louisville	Brown	May 16–19
1961	Fall	Chicago	Sherman	September 5–8
1962	Spring	Boston	Statler	May 15–18

* An international meeting jointly sponsored by the Division of Rubber Chemistry ACS, Committee D-11 of ASTM, and the Rubber and Plastics Division of ASME.

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1958

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ROBERT PRYOR (Hewitt-Robins, Inc.). Meeting dates in 1958: May 9—
International Rubber Group Meeting, General Brock Hotel, Niagara Falls,
Canada. June 10, October 14, December 2.

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1958: January 31, March 14, April 25, July 25, October 3, November 14,
December 19.

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(outing), September 25, December 4.

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GORDON RESEARCH CONFERENCES

The Gordon Research Conferences for 1958 will be held from 9 June to 29 August at Colby Junior College, New London, New Hampshire; New Hampton School, New Hampton, New Hampshire and Kimball Union Academy, Meriden, New Hampshire.

The Conferences were established to stimulate research in universities, research foundations and industrial laboratories. This purpose is achieved by an informal type of meeting consisting of scheduled lectures and free discussion groups. Sufficient time is available to stimulate informal discussions among the members of a Conference. Meetings are held in the morning and in the evening, Monday through Friday, with the exception of Friday evening. The afternoons are available for participation in discussion groups as the individual desires. This type of meeting is a valuable means of disseminating information and ideas which otherwise would not be realized through the normal channels of publication and scientific meetings. In addition, scientists in related fields become acquainted and valuable associations are formed which result in collaboration and cooperative effort between different laboratories.

It is hoped that each Conference will extend the frontiers of science by fostering a free and informal exchange of ideas between persons actively interested in the subjects under discussion. The purpose of the program is not to review the known fields of chemistry but primarily to bring experts up to date

as to the latest developments, analyze the significance of these developments, and to provoke suggestions as to underlying theories and profitable methods of approach for making new progress. In order to protect individual rights and to promote discussion, it is an established rule of each Conference that all information presented is not to be used without specific authorization of the individual making the contribution, whether in formal presentation or in discussion. No publications are prepared as emanating from the Conferences.

Individuals interested in attending a Conference are requested to send their applications to the Director. Each applicant must state the institution or company with which he is connected and the type of work in which he is most interested. Attendance at each Conference is limited to 100.

The complete program of the Conferences was published in "Science" for February 28th.

Requests for attendance at the Conferences, or for any additional information, should be addressed to W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. From June 9 to August 29, 1958 mail should be addressed to Colby Junior College, New London, New Hampshire.

<div align="center">Program for Elastomers Section</div>

<div align="center">*Colby Junior College, New London, New Hampshire*</div>

4 Aug. W. Postelnek, "Status of the High Temperature Polymer Program"; W. F. Watson, "Mechanico-Chemical Reactions of Polymers"; G. S. Trick, "Effects of Microstructure on Crystallization Rates of Elastomers."

5 Aug. M. Berger, "Kinematics of a Rolling Tire and its Application to Tire Performance"; D. C. Edwards and E. B. Storey, "The Union of Butyl Rubber with Carbon Black"; A. M. Gessler, "Attrition of Carbon Black: Effect on the Carbon Black and on its Reinforcing Properties in Rubber."

6 Aug. G. N. Welding, Subject to be Announced; R. L. Zapp, "New Vulcanization Studies with Butyl Rubber"; David Craig, D. E. Diller, R. B. Fowler, F. A. Regenass, E. H. Rowe, W. L. Semon, J. J. Shipman and H. Tucker, "Perdeuterio SN Rubber."

7 Aug. Maurice Morton and Alan Rembaum, "Some Aspects of Homogeneous Anionic Polymerization"; Paul Fugassi, "The Sorption of Benzene by Natural and Synthetic Polymeric Hydrocarbons"; Melvin Mooney, "The Rheology of Visco-Elastic Materials."

8 Aug. Henno Keskkula, J. A. Schmidt and J. G. Cobler, "Methods of Studying Rubber-Polystyrene Compositions."

<div align="right">Edwin B. Newton, *Chairman*
Paul G. Carpenter, *Vice Chairman*</div>

NEW BOOKS AND OTHER PUBLICATIONS

Ebonite: Its Nature, Properties, and Compounding. By J. R. Scott. Maclaren and Sons, Ltd., 131 Great Suffolk Street, London, S.E. 1, England. Hard cover, 6 × 9 inches, 293 pages. Price $8.00.—This is the first comprehensive book on the science of ebonite. The experimental work on which it is based was carried out under a scheme of Joint Ebonite Research, initiated in

1931, the cooperating organizations being the Research Association of British Rubber Manufacturers, the British Electrical and Allied Industries Research Association and the Ceylon Rubber Research Scheme.

A survey of the literature was first prepared and this showed a conspicuous lack of extensive systematic studies relating composition with properties. The plan of the Joint Ebonite Research was therefore to study systematically the dependence of the properties of ebonite on its composition, vulcanization, etc. The results of the investigation were first issued in the form of confidential reports to members of the cooperating societies and have subsequently mostly been published in scientific periodicals in a series of nearly 60 papers. The object of the present book is to bring together the main facts from these numerous papers and, where necessary, to discuss the results in the light of present knowledge.

The first nine chapters, occupying approximately half the book, are concerned with the nature of ebonite, the effect of rubber-sulfur ratio on properties, use of purified natural rubbers and gutta-percha, surface deterioration in light, resistance to swelling by liquids, and the various aspects of the vucanization process, namely, heat evolution during cure, time and temperature of cure, and method of curing. Five of the remaining chapters relate to the compounding of ebonite with accelerators and activators, mineral fillers including silica, ebonite dust, softeners and reclaimed rubber. There follows a chapter on synthetic rubber ebonites and a concluding chapter giving recommendations on compounding and curing. Test methods are described in an appendix and there is a bibliography and a subject index.

At the end of most chapters, concise conclusions are appended on the results of the work described in more detail in the chapter. This is a useful feature particularly for the busy reader wishing to acquire a rapid grasp of the essentials.

The object of the final chapter—recommendations on compounding and curing—is to bring together the many conclusions and recommendations given in earlier chapters on the best compounding and curing procedures for improving particular properties. The properties considered are as follows: quick curing (without excessive overheating), avoidance of deformation in open-steam cures, resistance to deformation at high temperatures, mechanical strength, low dielectric loss, resistance to light (surface deterioration), and resistance to water and organic liquids. The extension of this chapter to include examples of mixes for particular ebonite products would have been helpful to manufacturers, particularly those with little or no experience of ebonite production. [Reviewed in *Rubber Journal and International Plastics*.]

ZINC OXIDE REDISCOVERED. Prepared by Harvey E. Brown. Published by New Jersey Zinc Company, 160 Front Street, New York 38, New York. Hard cover, 8½ × 11¼ inches, 100 pages. Price $3.00.—This attractive book is perhaps the most comprehensive presentation of zinc oxide ever made, and those desiring over-all information on the subject in a semi-technical manner will find much value in it. A survey of the material is made by dividing the book into three sections: Established Properties of Zinc Oxide, Frontier Properties of Zinc Oxide, and Illustrative Applications.

In the first section thermal properties are among the subjects discussed, and several pages are devoted to the effects of zinc oxide in rubber in this respect. Some of the other topics are components and constitution, history of manufacture, and crystal structure.

In the part on frontier properties, devoted to those whose potential is of great current interest, the following properties, among many others, are analyzed in detail: semiconductor, solid-state reaction, ferrite, catalytic and chemical. This section, which comprises the major portion of the book, is of value for its specific information and suggestions for present and future uses.

In the section on applications, rubber is among those discussed with special attention given to passenger car tires, wire and cable insulation, rubber rolls for calenders, and silicone rubber. The extensive appendix is unusually useful as it breaks down the list of references by subject: components and constitution, history, thermal properties, chemical properties, and others. [Reviewed in *Rubber Age* (N.Y.).]

Research Memoranda from the Research Association of British Rubber Manufacturers: R. 397 EXAMINATION OF VARIOUS WHITINGS, LIMESTONES, AND PRECIPITATED CALCIUM CARBONATES AS RUBBER FILLERS. By R. C. Moakes, J. R. Pyne, and D. C. Soul. May 1954, 14 pages. R.399 MACKINTOSH TRIALS WITH PROOFINGS CONTAINING TRACES OF MANGANESE. May 1955, 3 pages. R.406 COMAPRISON OF WHITINGS AND PRECIPITATED CALCIUM CARBONATES AS FILLERS FOR NATURAL RUBBER. By J. R. Pyne. March 1957, 11 pages.— During the past few years the Research Association of British Rubber Manufacturers, in collaboration with the Research Council of the British Whiting Federation, has made an extensive study of whiting and other forms of calcium carbonate as fillers for natural rubber compounds, the results being recorded in two Research Memoranda, R.397 and R.406. The aim was to give guidance in selecting the type and grade of material (in particular, of natural whiting) best suited to the rubber manufacturer's needs, information which is of obvious value to both producer and user of this widely used class of filler.

The conclusions from this work are firstly that the behavior of calcium carbonate fillers in rubber depends largely on their fineness, most conveniently measured by specific surface; the finest (precipitated) materials have the greatest reinforcing power judged by the tensile and tear strengths and abrasion resistance of the rubber, although on the other hand they are more difficult to mix and give rubbers with lower resilience. The finer materials are generally more expensive to produce, and the relationships now established between particle size and rubber properties will help in choosing the appropriate balance between cost and performance. Surface treatment with fatty acids makes the very fine precipitated materials easier to mix and increases their reinforcing power, but has little effect on the behavior of coarser materials (with a smaller specific surface) such as ground natural whiting or limestone. The source of the chalk used in making whiting, *i.e.*, whether from the North or South of England deposits, and the method of grinding (wet or dry) do not appear to influence the behavior of the resulting whiting as a filler. The traces of manganese normally present in natural whiting show no evidence of impairing the aging properties of the rubber, a result in accord with the tests organized by the RABRM on the proofing of mackintosh fabrics with rubber compounds containing high and low manganese whitings, the results of which are described in Research Memorandum R.399. RABRM/4060.

A few copies of these three memoranda may be purchased for $.70 each from The Secretary, Research Association of British Rubber Manufacturers, Shawbury, Shrewsbury, Shropshire, England. One copy of each is on file in the Rubber Division Library at the University of Akron, Akron, Ohio.

CHEMISTRY OF NATURAL AND SYNTHETIC RUBBERS. By Harry L. Fisher. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, New York. Hard cover, 6 × 9 inches, 214 pages. Price $6.50.—The extent of the purely technical portion of the book is suggested by the following chapter headings: Vulcanization, Acceleration, Antioxidation and Antiozonation, Natural Rubber, Latex, Properties of Natural and Synthetic Rubbers, Synthetic Rubbers, Hard Rubber, Bonding Rubber to Metal, Reclaimed Rubber, and Chemical Derivatives. This is for the most part a book of facts with little sophisticated theory. Some recent work on the mechanism of sulfur vulcanization is described, however, and from this it is concluded that sulfur does not add chemically to a double bond, but is chiefly in the thio-ether linkage and on the alpha-methylene carbon. Vulcanization without elemental sulfur is discussed, and the mechanism of the various reactions, as far as they are known, is given.

A possible free radical mechanism is suggested as an explanation for the attack of rubber by oxygen. Antioxidants are represented as functioning as chain-terminating agents. Several types of antioxidants and antiozonants, such as N,N'-dialkyl-1,4-phenylene diamines, are listed. Synthetic rubbers, including the new "synthetic natural" rubbers (Ameripol SN and Coral Rubber), are discussed in regard to their synthesis, structure, properties, and raw material requirements. An unusual polymer described here is AXF synthetic rubber, a reaction product of benzene and ethylene dichlóride. The book concludes with a chapter on the chemical derivatives of natural and synthetic rubbers. Important reactions discussed are cyclization of rubber, hydrogenation, and chlorination.

This book is particularly recommended to the beginning rubber technologist or rubber chemist. It should also prove particularly useful to those persons connected with the rubber industry who are not chemists, but who must, in the course of their work, deal with chemists and chemical engineers. [Reviewed in *Rubber World*.]

RUBBER TRADE DIRECTORY OF GREAT BRITAIN: 1957–58. Published by Maclaren and Sons, Ltd., 131 Great Suffolk Street, London, S.E. 1, England. (Also available from *Rubber Age*, Book Department, 101 West 31st Street, New York 1, New York.) Hard cover, 6 × 9½ inches, 749 pages. Price $12.50.— This is the third edition of the Directory and has been completely revised and brought up-to-date. Following the pattern established in the earlier two editions, the Directory provides ready reference to rubber manufacturers and their products; suppliers of chemicals and compounding ingredients; suppliers of fabrics and textiles; suppliers of natural, synthetic scrap and reclaimed rubber, and a wealth of other information having to do with trade and research organizations, brand names, rubber technology courses, and a "who's who" of the industry. The table of contents and the subject index appear in English, French, German and Spanish, thus facilitating the Directory's use for Continental readers. A handsome publication, this directory provides much useful information on the rubber industry in Great Britain. [Reviewed in *Rubber Age* (N.Y.).]

ISO RECOMMENDATIONS

RUBBER CHEMISTRY AND TECHNOLOGY has been asked to publish some of the recommendations of the International Organization for Standardization (ISO). The American Standards Association, the U. S. Member, has given permission to publish R 33 through R 37 and R 48 as follows:

ISO Recommendation	R 33	March 1957

DU PONT CONSTANT LOAD METHOD OF MEASURING ABRASION RESISTANCE OF VULCANIZED NATURAL AND SYNTHETIC RUBBERS

FOREWORD

The world-wide use of the du Pont constant load method of measuring abrasion resistance and the absence of a recognized method whose results correlate with wear in service justify the standardization of those features of the du Pont method on which agreement has been reached in the last three years.

Some improved methods, now used experimentally, may be internationally agreed upon in a few years' time. Meanwhile, there is much to be gained by standardizing the du Pont method as far as possible. Close relation between the test results and service performance is not, however, necessarily implied.

An alternative method of test, using very similar apparatus and procedure, but imposing constant torque on the sample-holder instead of constant load, will be considered for recommendation when further experimental evidence has been received.

STANDARD COMPARISON RUBBERS

According to the type of rubber to be tested, one of the following two standard rubber compounds is selected for comparison: either the high quality tire tread type or the footwear sole and heel type.

A high standard of mixing technique should be employed in the preparation of these compounds, to ensure proper dispersion of the ingredients.

The compounds are:

"A" tire tread type standard compound

Natural rubber first-grade smoked sheet	100
Zinc oxide	5
Stearic acid	3
EPC black	50
Benzothiazolyl disulfide	1
Sulfur	3
Phenyl-2-naphthylamine	1

Vulcanization: 40 minutes at 144° C

"B" footwear sole and heel type standard compound

Natural rubber first-grade smoked sheet	100
Zinc oxide	4
Stearic acid	3
Di-(2-ethyl hexyl)phthalate	3
EPC black	60
Whiting	60
Mercaptobenzothiazole	1
Sulfur	3
Phenyl-2-naphthylamine	1

Vulcanization: 40 minutes at 153° C

TESTPIECE

Two testpieces are tested at the same time and compared with two test-pieces of the appropriate standard rubber. The pieces should be either 2 cm ± 0.05 cm or 0.8 inch ± 0.02 inch square and approximately either 1 cm or 0.4 inch thick, with suitable lugs for fixing in the sample-holder.

If desired, a small sample 2 cm × 2 cm × 0.5 cm or 0.8 inch × 0.8 inch × 0.02 inch may be prepared from a finished product or cut out with dies from molded sheet and attached by cold vulcanizing solution to the base portion of a worn down used testpiece, for test purposes.

APPARATUS

A disk which carries an abrasive surface is mounted on a shaft and rotated at a uniform speed within the range from 34 rpm to 40 rpm. The provision of a revolution counter is desirable.

The testpieces from the same compound are mounted, with their 2 cm or 0.8 inch square faces on the abrasive, on a bar, diametrically disposed across the disk so that the center of each sample is either 6.25 cm or 2.5 inches from the center of rotation.

The samples are held in contact with the abrasive by a force of either 3.62 kg or 8 lb weight by any suitable means free from friction and able to follow axial movement of the sample-holder as wear takes place. (If the abrasive disk is horizontal, dead weight can be used; if the abrasive disk is vertical, a wire led through a central hole in the shaft with a weight of either 3.62 kg or 8 lb attached at the rear can be used, as in the current design of the du Pont machine.)

A lever arm attached to the sample-holder is provided with means (weights and/or a spring balance) to restrain rotation and enable measurement of frictional torque to be made, if desired.

The abrasive is in the form of an annular disk of either 16.5 cm or 6.5 inches outside diameter with a central hole of either 7 cm or 2.75 inches in diameter for fixing the disk to the rotating member.

Silicon carbide abrasive grains mounted on stiff paper (see appendix) have been found to be suitable and the paper backing should have the following characteristics:

(a) The weight or paper substance should be at least 224 g/sq m with a tolerance of ± 5 per cent;
(b) The paper and the glue used to bond the abrasive grains should be waterproof so that a minimum of softening occurs under moist conditions[1].

Papers should be capable of at least 6 hours useful life and should generally be discarded when the rate of weight loss from the standard compound has fallen by about 10 per cent, but not more, of the rate of loss at the first measuring after the running-in period (20–30 minutes—see Procedure). The rate of loss of cutting power is dependent on the compound being tested, high-grade carbon black compound causing much less loss of cut than lower-grade compounds containing whiting or hard mineral fillers.

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[1] It is not recommended that the test should be performed in a relative humidity greater than 90 per cent.

The abrasive surface is continuously cleaned by means of air jets, directed on the working surface at two positions between the samples. The air supply is at a pressure of not less than either 1.75 kg/sq cm or 25 lb/sq in and free from oil or water. On each side there is a set of jets radially disposed and consisting of three 1 mm or 0.04 inch holes, 6 mm or 0.25 inch apart, arranged to leave a space of about 6 mm or 0.25 inch between the jets and the surface of the abrasive. (The addition of stiff bristle brushes, set at an angle to the track, is advantageous in some circumstances, but their use is optional.)

PROCEDURE

Preparation and conditiong of testpieces follows the general procedure adopted for all physical tests, as regards interval between vulcanization and testing, and conditions of storage.

Mounting of the testpieces in the holder is carried out without undue distortion of the abraded surface, but with no possibility of movement of the testpiece on the bar or the sample-holder.

A running-in period to give even seating of the samples on the abrasive should be made without weighing, and in the case of a new abrasive disk, it is preferable to use the first 20 minutes for running-in samples, before weighed tests begin. Change of cutting power appears to be less rapid after this initial period.

Samples replaced for successive runs should be arranged to rub in the same direction on the abrasive.

Systematic reversal of order in a set of tests to overcome bias due to gradual change of abrasive cutting power or random distribution of test runs of pairs of testpieces should be employed.

The duration of any one test is recorded in terms of revolutions of the abrasive rather than time.

It should be arranged that the duration of test is adjusted so that a roughly equal amount of rubber is abraded from each of the test rubbers and the standard. This is desirable, as there is some evidence for a systematic effect on the weight loss of the amount of sample projecting from the clamp bar.

A useful discarding point for the samples is when approximately 0.3 cm or 0.125 inch has been abraded away, that is, about half the projecting height above the clamp.

The volume losses are derived from the weight losses by dividing the latter by the density of the particular sample, determined by the usual weight in air and water method, either before commencing abrasion tests or on the remaining rubber after completing the tests.

The repetition of density determinations on duplicate samples from one batch may be dispensed with but is a useful check on uniformity and possible errors due to accidental confusion of a series of samples of similar appearance.

TEMPERATURE OF TEST

The test is carried out at a standard laboratory temperature.

EXPRESSION OF RESULTS

Results are expressed as a figure of merit or abrasion resistance index of which higher values denote better performance, derived as follows:

$$\text{Abrasion resistance index} = \frac{S}{T} \times 100$$

where S = volume loss, in milliliters per 1000 revolutions of the abrasive, from the appropriate standard compound (which should be stated as either standard "A" or standard "B"), and T = volume loss, in milliliters per 1000 revolutions of the abrasive, from the testpieces of the sample rubber.

The values of S and T, as well as the type of abrasive used and the temperature of test, should be stated.

APPENDIX

NOTE ON ABRASIVE PAPERS FOR THE DU PONT TEST

This note has been added to serve as a guide in the choice of a suitable abrasive paper, in view of the difficulty of defining the paper in internationally acceptable terms.

1. The silicon carbide grain size is known commercially as 180, in the widely used system for specifying abrasive grains. The system is empirical, and no correlation exists between these numbers and the nominal apertures of the sieves expressed in microns.

2. We understand that many factors are involved in the control of manufacture of a satisfactory abrasive paper, which are difficult to define. These include the shape of the particles, their orientation on the paper, the density of deposition and the degree to which they are embedded in the glue or resin support.

It is necessary to refer at present to a commercial specification of a paper which has been found satisfactory:

Wetordry Tri-M-ite 180 E

from the Minnesota Mining and Manufacturing Company.

3. It has been found that there are variations between batches of paper of the same nominal characteristics, which are undesirable in a standardized test. To overcome this, the manufacturers have offered to make a large uniform batch with the desired characteristics and hold this at the disposal of laboratories wishing to undertake the ISO test.

The behavior of subsequent supplies should be compared with that of the first supply.

Arrangements have been made for the supply of this material from the United Kingdom branch of Minnesota Mining and Manufacturing Company, Arden Road, Adderley Park, Birmingham 8. The paper should be referred to as *Special ISO Batch*, when ordering.

If a member country wishes to manufacture it locally, samples of the standard series of paper can be sent and may be reproduced at will by local laboratories.

By agreement between the parties, any other abrasive paper manufactured in any country may be used, provided its properties are sufficiently near to those of the *Special ISO Batch* for the test forming the basis of this Recommendation.

DETERMINATION OF TEAR STRENGTH OF VULCANIZED NATURAL AND SYNTHETIC RUBBERS (CRESCENT TESTPIECE)

SUMMARY

The test consists in inserting a slit of accurate depth in a special testpiece and measuring the force required to tear across the width of the unnicked portion.

TESTPIECE

The testpiece conforms to the shape of the die shown in Figure 1. The dimensions of the die are as given in Table I. The testpiece is cut from a sheet
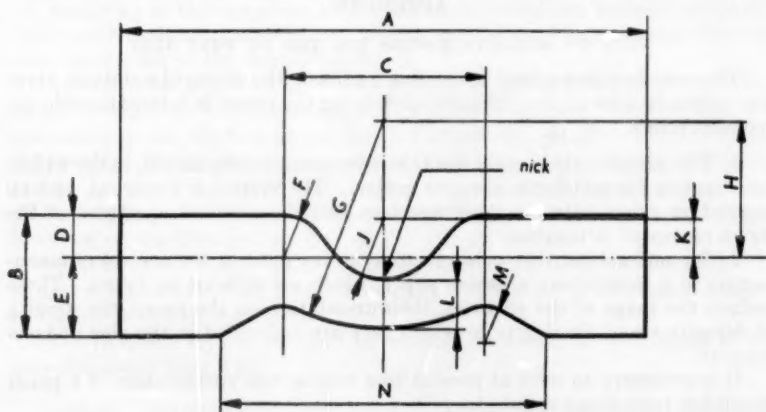
FIG. 1.

by punching with the die using a single blow of a mallet or (preferably) a single stroke of a press; the rubber may be wetted with water or a soap solution and should be supported on a sheet of slightly yielding material (e.g., leather, rubber belting or cardboard) on a flat, rigid surface.

TABLE I

DIMENSIONS OF TESTPIECE

Dimension	Millimeters	Inches	Dimension	Millimeters	Inches
A	110	4.3	G	43.2	1.7
B	25	1	H	29	1.14
C	45	1.80	J	12.5	0.5
D	9	0.375	K	8.5	0.34
E	16	0.625	L	10.2	0.4
F	9	0.375	M	7.5	0.3
			N	68	2.7

The tear strength is particularly susceptible to grain effects in vulcanized rubber. Normally, all testpieces are prepared with the grain at right angles to their length, but in cases where grain effects are significant and are to be evaluated, two sets of testpieces are cut from the sheet, at right angles, and parallel to the grain.

The thickness of the testpiece should not fall outside the limits of either 1.8 mm to 2.8 mm or 0.07 inch to 0.11 inch and should be measured by means of a micrometer gage having a pressure foot approximately 6 mm or 0.25 inch in diameter which exerts a pressure of either 200 g/sq cm or 3 lb/sq in on the rubber. At least three gage readings are taken in the region of test. If an odd number of readings is taken, the value to be used is the middle value. If an even number of readings is taken, the value to be used is the average of the middle two readings. No reading should deviate by more than 2 per cent from the value to be used.

Tests intended to be comparable are made on testpieces not varying in thickness by more than ± 7.5 per cent from the mean. In addition, the width of the testpiece below the nick is measured because it is necessary to correct the final result for both the width and thickness of the testpiece[1].

A single nick or slit of depth of either 0.50 mm ± 0.08 mm or 0.020 inch ± 0.003 inch is cut with extreme care and accuracy across the center of the concave inner edge of the testpiece.

APPARATUS

The essentials of the method for introducing the nick are as follows:

The testpiece is clamped firmly in a vertical plane, especially in the region where the nick is introduced. The cutting is done by means of a razor blade clamped in a vertical plane at right angles to the testpiece. Either the razor blade-holder is fitted with guides to ensure an exact horizontal motion over the testpiece and is supported in a manner which permits no lateral motion of the razor blade, or the blade is supported in a stationary holder, and the clamped testpiece mounted on guide rails which ensure an exact horizontal motion without any lateral movement. In both cases, the guides are such as to ensure accurate centering of the nick. The cutter is fitted with a micrometer gage for controlling the depth of the nick and is calibrated for each blade. The height of the blade-holder and/or the clamped testpiece is adjusted for each blade by cutting one or two preliminary nicks, and measuring these by means of a microscope. The blade may be wetted with water or a soap solution during the nicking, and any testpieces having a depth of nick outside the limits of either 0.42 mm to 0.58 mm or 0.017 inch to 0.023 inch are discarded. A suitable apparatus for nicking tear testpieces (the IRI tear cutter) has been described[2].

The testpiece is stretched in a tension-testing machine capable of substantially constant rate of traverse of the moving grip. This rate is between either 450 mm/min and 550 mm/min or 18 in/min and 22 in/min.

PROCEDURE

The testpiece is stretched in the tension-testing machine; stretching is not interrupted before the testpiece breaks. The maximum load reached during the tearing is noted.

At least three, and preferably six testpieces are tested.

TEMPERATURE OF TEST

The test is normally carried out at a standard laboratory temperature, but it should be remembered that some synthetic rubbers have markedly lower tear strengths at elevated temperatures, and hence tests may also have to be carried out at high temperatures, 100° C being a useful temperature.

EXPRESSION OF RESULTS

The property depends upon the width and thickness of the testpiece, and the result is expressed as the load necessary to tear a testpiece of standard width and thickness. The value is stated in units of force, F.

$$F = \frac{L \times W_1 \times t_1}{W_2 \times t_2}$$

where L = load in kilograms or pounds
W_1 = width of standard testpiece = 9.7 mm = 0.38 inch
W_2 = width of actual testpiece
t_1 = thickness of standard testpiece = 2.5 mm = 0.10 inch
t_2 = thickness of actual testpiece.

The result reported is the middle value, if an odd number of testpieces is used, or the average of the middle two values, if an even number of testpieces is used, the various results being classified in order of increasing values. If only three testpieces are tested, then the individual results of each are given. The temperature of test is stated.

REFERENCES

[1] Buist, *Trans. Inst. Rubber Ind.* 20, 155 (1945).
[2] Buist and Kennedy, *India Rubber J.* 110, 809 (1946).

ISO Recommendation   **R 35**   **March 1957**

DETERMINATION OF THE MECHANICAL STABILITY OF LATEX

FOREWORD

This method of test is for natural rubber latex which contains preservative agents, and which has been submitted to some type of concentration process. The test is not necessarily suitable for latexes from natural sources other than Hevea brasiliensis or for latexes of synthetic rubber, compounded latex, vulcanized latex or artificial dispersions of rubber.

SUMMARY

Latex is stirred at a high speed and the time required to produce obvious signs of clotting is regarded as a measure of mechanical stability.

APPARATUS

A latex container consisting of a flat-bottomed cylindrical vessel either 127 mm or 5 inches high and having an inside diameter of either 56 mm to 60 mm or 2.20 inches to 2.35 inches. The inner surface must be smooth and a transparent container is preferred.

The stirring apparatus consists of a vertical stainless steel shaft either 15.2 cm or 6 inches long and tapering to either 6.35 mm or 0.25 inch at its lower end, where is attached a horizontal smooth stainless steel disk either 21 mm ± 0.025 mm or 0.820 inch ± 0.001 inch in diameter and either 1.55 mm ± 0.05 mm or 0.062 inch ± 0.002 inch thick by means of a threaded stud at the exact center of the disk. The apparatus is designed to maintain a stirring speed of 14,000 rpm ± 200 rpm throughout a test. The speed should be

checked while a test is in progress.   At this speed the shaft must not run more than either 0.25 mm or 0.01 inch out of true.

An arrangement for holding the latex container so that the axis of the rotating shaft is concentric with that of the latex container and the bottom of the stirring disk is either 12.5 mm ± 2.5 mm or 0.5 inch ± 0.1 inch from the bottom inside of the latex container.

PROCEDURE

The latex is diluted with 1.6 per cent NH_3 to 55 per cent ± 0.2 per cent total solids.   It is strained through square mesh stainless steel gauze with a nominal aperture width of 0.160 mm to 0.200 mm.   Within 6 hours, 80 g ± 1 g of the diluted, strained latex is weighed into the container and the temperature adjusted to 35° C ± 1° C.   The latex should not be subjected to unnecessarily prolonged warming tending to form a surface skin by evaporation.   A convenient method of obtaining the required temperature is by passing hot water through a glass tube bent to a suitable shape and very gently stirring the latex with it for about 5 minutes, while still in the container.

The container is placed in position and the contents stirred at 14,000 rpm ± 200 rpm until the end point is reached.

The end point is reached, when small pieces of coagulated rubber are first readily seen in the thin film of liquid formed when a glass rod is dipped into the latex and lightly drawn over the palm of the hand, or when a curdy or rippled appearance is first visible over most of the surface of the latex in the container.

In case of dispute the end point is reached when, on straining the latex through stainless steel gauze, with a nominal aperture width of 0.160 mm to 0.200 mm, the amount of dry coagulum obtained first exceeds 0.5 g.

EXPRESSION OF RESULTS

In reporting the result of the test, the end point used should be stated.

The mechanical stability of the latex is expressed as the number of seconds between the commencement of stirring and the end point.   The results of duplicate tests should not differ by more than 5 per cent.

ISO Recommendation　　　　　　**R 36**　　　　　　　**March 1957**

DETERMINATION OF THE ADHESION OF VULCANIZED NATURAL OR SYNTHETIC RUBBERS TO TEXTILE FABRICS

FOREWORD

The methods of test described below cover the procedure of measuring the force required to separate, by stripping, two plies of fabric bonded with rubber, or a rubber layer and a fabric ply.   They are applicable when the ply surfaces are approximately plane or cylindrical as in the case of belting, insertion sheet, hose and tire carcasses.   For surfaces which contain sharp bends, angles or other gross irregularities that cannot be avoided, special methods must be employed.

SUMMARY

The test consists in measuring the force required to separate, by stripping, two plies of fabric bonded with rubber, or a rubber layer and a fabric ply of standard dimensions in the form of a flat strip or a cylinder.

DIMENSIONS OF TESTPIECE

(a) *Strip testpiece.*—The testpiece is either 25 mm ± 0.5 mm or 1 inch ± 0.02 inch wide and of sufficient length to allow a minimum test length of either 100 mm or 4 inches. The thickness of the ply or layer which is to be separated should not exceed either 6 mm or 0.25 inch. Where the ply or layer which is to be separated exceeds either 6 mm or 0.25 inch, it should be cut down to the requisite thickness before proceeding with the test. The thickness of this ply should be no greater than the thickness of the remainder.

(b) *Ring testpiece.*—Hose testpieces are either 25 mm ± 0.5 mm or 1 inch ± 0.02 inch long cylinders. Rings having an internal diameter in excess of either 100 mm or 4 inches are cut through and opened to form strip testpieces. The thickness of the ply or layer which is to be separated should not exceed either 6 mm or 0.25 inch. Where the ply or layer which is to be separated exceeds either 6 mm or 0.25 inch, it should be cut down to the requisite thickness before proceeding with the test. The thickness of this ply should be no greater than the thickness of the remainder.

APPARATUS

The testing machine should be of the pendulum single lever type capable of a substantially constant rate of traverse of the moving head. It must be able to maintain the specified rate of traverse during the test. The apparatus should preferably be fitted with an autographic recorder.

Note.—A machine having a pendulum with a large moment of inertia is unsuitable for this test.

METHOD OF TEST

(a) In the case of a flat strip, the outer layer of rubber (if any) and the ply are separated for a distance of approximately 75 mm or 3 inches. Separated ends of the testpiece are fixed in the grips of the testing machine. The rate of travel of the power-driven grip is constant and within the range of either 5 cm/min to 25 cm/min or 2 in/min to 10 in/min so as to give a ply separation of either 2.5 cm/min to 12.5 cm/min or 1 in/min to 5 in/min. The machine is operated without the use of any device for maintaining maximum load indication.

During the separation, readings are taken of the load at intervals of either 12.5 mm or 0.5 inch over a distance of either 100 mm or 4 inches. The average load is preferably determined from an autographic record, the area of the record being ascertained by a planimeter (neglecting the beginning and the end of the diagram) and this area divided by the length of the base.

(b) In the case of rings, the procedure and conditions are as described above, except that the grip attached to the head of the machine is replaced by a freely rotating mandrel having an outside diameter substantially the same as the inside diameter of the testpiece and that the rate of travel of the power-driven grip is either 2.5 cm/min to 12.5 cm/min or 1 in/min to 5 in/min. The mandrel is mounted so that the stripping force is applied at right angles to the axis of rotation.

NUMBER OF TESTPIECES

Duplicate testpieces are tested.

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The test is normally carried out at a standard laboratory temperature and humidity.

EXPRESSION OF RESULTS

The adhesion value is expressed as the average force in kg/cm width or lb/in width, required to cause separation of the plies at either 2.5 cm/min to 12.5 cm/min or 1 in/min to 5 in/min. The results are the average for the duplicate testpieces, where an autographic record is taken. Where readings are taken at 12.5 mm or 0.5 inch intervals, the average of the sixteen results is taken. The type of testpiece used and the temperature of test are stated.

ISO Recommendation	R 37	March 1957

DETERMINATION OF TENSILE STRESS-STRAIN PROPERTIES OF VULCANIZED NATURAL AND SYNTHETIC RUBBERS

SUMMARY AND EXPLANATORY NOTE

In this test, standard testpieces, either rings or dumbbells as described below, are stretched until they break in a tension-testing machine capable of a substantially constant rate of traverse of the lower grip or pulley.

Ring and dumbbell testpieces do not necessarily give the same values for the stress-strain properties; this is due mainly to the fact that in stretched rings the stress is not uniform over the cross-section; a second factor is the existence of "grain", which may cause dumbbells to give different values according as their length is parallel or perpendicular to the grain.

Rings give lower, sometimes much lower, tensile strength values than dumbbells, the latter being much nearer to the true tensile strength of the rubber. The estimation of true tensile strength from ring data involves extrapolation of the stress-strain curve[1].

TESTPIECE

The testpiece is either a ring or a dumbbell, described as follows:

(a) *Ring testpiece.*—Rings are nominally of internal diameter either 44.6 mm or 1.76 inches and external diameter either 52.6 mm or 2.07 inches, the radial width nowhere deviating by more than either ± 0.2 mm or ± 0.008 inch from the mean width. The thickness is preferably between either 4 mm

Die

Fig. 1.

xxiii
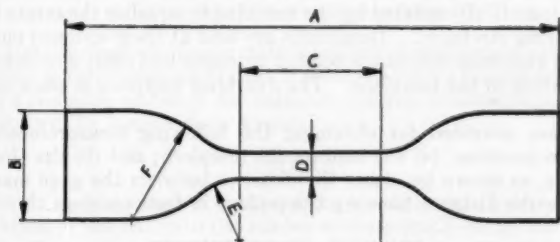
and 6 mm or 0.16 inch and 0.24 inch; in any one ring the thickness must nowhere deviate by more than either ± 0.2 mm or ± 0.008 inch from the mean thickness.

(b) *Dumbbell testpiece.*—The testpiece is determined by the die dimensioned as given in Figure 1 and Table I. The testpiece must not be more than either

TABLE I
DIMENSIONS OF TESTPIECE

Dimension	Millimeters	Inches
A Overall length, minimum	115	4.5
B Width of ends	25 ± 1	1.00 ± 0.04
C Length of narrow parallel portion	33 ± 1	1.312 ± 0.040
D Width of narrow parallel portion*	6 + 0.4	0.25 + 0.002
	− 0.0	− 0.014
E Small radius	14 ± 0.5	0.562 ± 0.020
F Large radius	25 ± 1	1.00 ± 0.04

* The variation in any one die should not exceed either 0.05 mm or 0.002 inch.

3 mm or 0.12 inch thick. The gage marks are not more than either 25 mm or 1 inch apart and are equidistant from the ends of the central parallel-sided part of the testpiece.

MEASUREMENT OF TESTPIECES

(a) *Ring testpieces.*—Thickness is measured by a micrometer gage, the foot of which exerts a pressure of either 200 g/sq cm or 3 lb/sq in on the rubber. The width is measured in the same way, but using a gage with curved feet to fit the curvature of the ring. For precise work, the cross-section of the ring is calculated from its weight, density and mean circumference; for the ring specified in 2 (a):

$$\pi \times 48.6 = 152 \text{ mm or } 6.00 \text{ inches.}$$

(b) *Dumbbell testpieces.*—Thickness is measured by a gage as described in 3 (a). The width of the test portion is assumed to be equal to the width between the cutting edges of the narrow central part of the die; for this purpose, the width of this part of the die is measured to the nearest 0.05 mm or 0.002 inch.

APPARATUS

The tensile test machine is capable of a substantially constant rate of traverse of the moving grip or pulley. This rate is between either 45 cm/min and 55 cm/min or 18 in/min and 22 in/min. Rings are fitted over two rotatable pulleys, either 25 mm or 1 inch in diameter, at least one of which, preferably the lower, is automatically rotated by the machine to equalize the strain in the ring while it is being stretched. Dumbbells are held at their widened ends in grips that tighten automatically as the tension increases and exert a uniform pressure across the width of the testpiece. The dumbbell testpiece is place centrally in the grips.

Means are provided for obtaining the following measurements without stopping the machine: (a) the load on the testpiece; and (b) the elongation of the testpiece, as shown by either the distance between the gage marks on the dumbbell, or the distance between the pulleys in tests on rings.

NUMBER OF TESTPIECES

At least three pieces are tested.

Tests are usually carried out at a standard laboratory temperature. The testpieces are conditioned at the test temperature for not less than 12 hours immediately before testing.

EXPRESSION OF RESULTS

In tests on rings, the calculation of modulus or elongation at constant stress is made on the *mean* circumference, but the elongation at break is calculated on the *internal* circumference.

For tensile strength, elongation at break, modulus or elongation at constant stress, the result reported is: the middle value, if an odd number of testpieces is used, or the average of the middle two values, if an even number of testpieces is used, the various results being classified in order of increasing values.

The report should include: (*a*) the values, determined as described above, for tensile strength, elongation at break, and modulus or elongation at constant stress; (*b*) type of testpiece used; (*c*) method of determining cross-section (of rings); (*d*) number of testpieces used; (*e*) temperature of test; (*f*) direction of grain (for dumbbells).

REFERENCE

¹ Reece, *Trans. Inst. Rubber Ind.* 11, 312 (1935); Scott, *J. Rubber Research* 18, 30 (1949).

ISO Recommendation   **R 48**   July 1957

DETERMINATION OF HARDNESS OF VULCANIZED NATURAL AND SYNTHETIC RUBBERS

FOREWORD

The standard hardness test is based on a measurement of the penetration of a rigid ball into the rubber testpiece under specified conditions. The measured penetration is converted into International Rubber Hardness Degrees (IRH), the scale of degrees being so chosen that 0 represents a material having an elasticity modulus of zero and 100 represents a material of infinite elasticity modulus, and so that the following conditions are fulfilled over most of the normal range of hardness:

(*a*) One International Rubber Hardness Degree always represents approximately the same proportionate difference in Young's modulus;

(*b*) Readings in International Rubber Hardness Degrees are approximately the same as those of the Shore durometer types "A".

For substantially elastic isotropic materials like well-vulcanized natural rubbers, the hardness in International Rubber Hardness Degrees bears a known relation to Young's modulus, although for markedly plastic or anisotropic rubbers the relationship will be less precisely known.

SUMMARY

The hardness test consists in measuring the difference between the depths of penetration of the ball into the rubber under a small initial load and a large final load. From this difference the hardness in International Rubber Hardness Degrees is derived by using either Table II, page xxvii, or the graph based on this table, or a scale, reading directly in International Rubber Hardness

Degrees and derived from the table, fitted to the penetration-measuring instrument.

The relation between the difference of penetration and the hardness expressed in International Rubber Hardness Degrees is based on:

(1) The known approximate relation, for a perfectly elastic isotropic material, between penetration P (in hundredths of a millimeter) and Young's modulus M (in kilograms-force per square centimeter), namely

$$*F/M = 0.00017\ R^{0.65}\ P^{1.35}$$

where F = indenting force (kgf), R = radius of ball (cm).

(2) The use of a probit (integrated normal error) curve to relate $\log_{10} M$ and the hardness in International Rubber Hardness Degrees, as shown in the diagram on page 7, this curve being defined thus:

(a) value of $\log_{10} M$ corresponding to midpoint of curve
= either 1.37 (M expressed in kgf/sq cm) or 2.52 (M expressed in lb/sq in), i.e., M = 23.3 kgf/sq cm or 330 lb/sq in

(b) maximum slope
= 57 International Rubber Hardness Degrees per unit increase in $\log_{10} M$

TESTPIECE

The testpiece has its upper and lower surfaces flat, smooth and parallel to one another, two pieces of rubber (but not more than two) may be superposed to obtain the necessary thickness.

TABLE I

Total thickness of test piece		Minimum distance from point of impact to edge of testpiece	
Millimeters	Inches	Millimeters	Inches
2.5	0.1	6.5	0.25
5	0.2	7.6	0.3
8	0.3	9.0	0.35
10	0.4	10.0	0.4
15	0.6	11.5	0.45
25	1.0	12.7	0.5

The standard testpiece is between 8 mm and 10 mm thick, the lateral dimensions being such that no test is made at a distance from the edge of the testpiece less than the appropriate distance shown in Table I hereunder.

Non-standard testpieces may be thicker or thinner than the standard, but in no case less than 2 mm thick. The lateral dimensions are such that no test is made at a distance from the edge less than the appropriate distance shown in Table I hereunder.

Tests intended to be comparable must be made on testpieces of the same thickness.

APPARATUS

The essential parts of the apparatus are:

(a) A vertical plunger terminating in a rigid ball 2.44 mm ± 0.06 mm in diameter;

(b) Means for applying loads of 30 g and 570 g ± 5 g to the ball; it is essential to allow for the weight of the plunger and of any fitting at-

TABLE II

D 0.01 mm	International Rubber Hardness Degrees	D 0.01 mm	International Rubber Hardness Degrees	D 0.01 mm	International Rubber Hardness Degrees	D 0.01 mm	International Rubber Hardness Degrees
0	100	50	71.0	100	48.8	150	35.6
1	100	51	70.4	101	48.5	151	35.4
2	99.9	52	69.8	102	48.1	152	35.2
3	99.8	53	69.3	103	47.8	153	35.0
4	99.6	54	68.7	104	47.5	154	34.8
5	99.3	55	68.2	105	47.1	155	34.6
6	99.0	56	67.6	106	46.8	156	34.4
7	98.6	57	67.1	107	46.5	157	34.3
8	98.1	58	66.6	108	46.2	158	34.1
9	97.7	59	66.0	109	45.9	159	33.9
10	97.1	60	65.5	110	45.6	160	33.7
11	96.5	61	65.0	111	45.3	161	33.5
12	95.9	62	64.5	112	45.0	162	33.3
13	95.3	63	64.0	113	44.7	163	33.2
14	94.7	64	63.5	114	44.4	164	33.0
15	94.0	65	63.0	115	44.1	165	32.8
16	93.4	66	62.5	116	43.8	166	32.7
17	92.7	67	62.0	117	43.5	167	32.5
18	92.0	68	61.5	118	43.3	168	32.3
19	91.3	69	61.1	119	43.0	169	32.2
20	90.6	70	60.6	120	42.7	170	32.0
21	89.8	71	60.1	121	42.5	171	31.9
22	89.2	72	59.7	122	42.2	172	31.7
23	88.5	73	59.2	123	41.9	173	31.6
24	87.8	74	58.8	124	41.7	174	31.4
25	87.1	75	58.3	125	41.4	175	31.3
26	86.4	76	57.9	126	41.1	176	31.1
27	85.7	77	57.5	127	40.9	177	31.0
28	85.0	78	57.0	128	40.6	178	30.9
29	84.3	79	56.6	129	40.4	179	30.7
30	83.6	80	56.2	130	40.1	180	30.6
31	82.9	81	55.8	131	39.9	181	30.5
32	82.2	82	55.4	132	39.6	182	30.3
33	81.5	83	55.0	133	39.4	183	30.2
34	80.9	84	54.6	134	39.1	184	30.1
35	80.2	85	54.2	135	38.9	185	30.0
36	79.5	86	53.8	136	38.7	186	29.9
37	78.9	87	53.4	137	38.4	187	29.8
38	78.2	88	53.0	138	38.2	188	29.6
39	77.6	89	52.7	139	38.0	189	29.5
40	77.0	90	52.3	140	37.8	190	29.4
41	76.4	91	52.0	141	37.5	191	29.3
42	75.8	92	51.6	142	37.3	192	29.2
43	75.2	93	51.2	143	37.1	193	29.1
44	74.5	94	50.9	144	36.9	194	29.0
45	73.9	95	50.5	145	36.7	195	28.9
46	73.3	96	50.2	146	36.5	196	28.8
47	72.7	97	49.8	147	36.2	197	28.8
48	72.2	98	49.5	148	36.0	198	28.7
49	71.6	99	49.1	149	35.8	199	28.6
						200	28.5

tached to it and for the force of any spring acting on it, in order that the loads *actually applied to the ball* shall be as specified;

(c) Means, e.g., a dial gage, for indicating the movement of the plunger, either in metric or in inch units or reading directly in International Rubber Hardness Degrees;

(d) A foot about 20 mm in diameter, normal to the axis of the plunger and having a central hole about 5 mm in diameter for the passage of the plunger, the foot forming part of the penetration-measuring gage; the foot rests on the testpiece and exerts a pressure on it of 200 g/sq cm 300 g/sq cm;

(e) Means, e.g., an electrically operated buzzer, for gently vibrating the apparatus to overcome any slight friction (this can be omitted in to instruments where friction is completely eliminated).

PROCEDURE

The testpiece is first conditioned. The upper and lower surfaces of the testpiece are slightly dusted with talc and the testpiece supported on a horizontal rigid surface. The foot is first lowered so as to rest on the surface of the testpiece. The plunger and indenting ball are pressed for 5 seconds vertically on to the rubber, the load on the ball being 30 g.

If the gage is graduated directly in International Rubber Hardness Degrees, the bezel of the gage is then turned so that the pointer indicates 100 (care being taken not to exert any vertical pressure on the gage). An additional load of 540 g $\pm$ 5 g is then applied and maintained for 30 seconds, the reading on the gage is the hardness in International Rubber Hardness Degrees.

During the loading periods the apparatus is gently vibrated to overcome any friction.

If the gage is graduated in metric or in inch units, the movement D (in hundredths of a millimeter) of the plunger caused by applying the additional 540 g load as described above is read off and converted into International Rubber Hardness Degrees by using Table II, or the graph constructed therefrom.

NUMBER OF READINGS

One measurement is made at each of four different points distributed over the testpiece and the results averaged.

CONDITIONING

The samples are maintained at the temperature of test and at a relative humidity, still to be agreed, for at least twelve hours immediately before testing.

TEMPERATURE OF TEST

The test is normally carried out at a standard laboratory temperature.

EXPRESSION OF RESULTS

Hardness is reported to the nearest whole number as the mean of the four measurements expressed in International Rubber Hardness (IRH) Degrees, and the following additional data are quoted:

(a) thickness of testpiece,
(b) temperature of test.
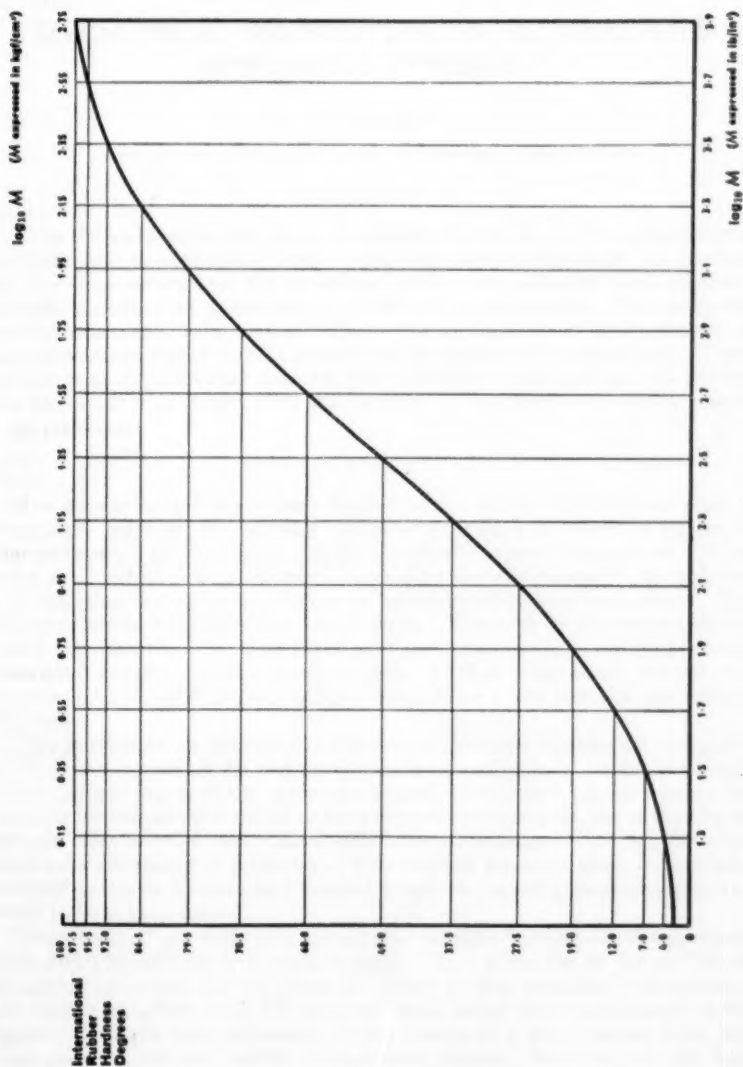
MECHANICAL PROPERTIES OF NATURAL AND SYNTHETIC RUBBERS *

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INTRODUCTION

It is the purpose of this paper to investigate the mechanical properties of synthetic and natural rubber under relatively small elongations. In particular, it will be shown how the measured tensile creep data for these materials explains the observed hysteresis and heat build up properties. The molecular mechanisms responsible for these effects will be pointed out and methods for improvement in regard to heat production properties will be examined. Comparison with experimental data for polybutadiene, synthetic natural rubber, and high molecular weight SBR will be made in an effort to check the general ideas presented.

THEORY

If a tensile force F is suddenly applied to the end of a rectangular piece of amorphous polymer, the polymer elongates with time as shown in Figure 1[1]. The time scale in this figure depends markedly upon temperature. If the point A is reached at a time of one minute after the load is applied, the polymer is so cold that the molecular chains do not slip readily over each other. The polymer therefore behaves like a solid glass. However, as the temperature is raised, the chains acquire more freedom of motion and at high enough temperatures point B will be reached in one minute. At that temperature the polymer appears to be a "slow" rubber which is hard under a fast test and soft under a slow test.

The portion BC of the curve in Figure 1 is the quasi equilibrium elongation of the polymer network formed by the chain entanglements. Since the height of this plateau region of the curve can be used to calculate a quasi equilibrium modulus for the network set up in the polymer by entanglements of the chains, one can calculate the molecular weight between entanglements M_e, from the usual network theory of elasticity. This method for calculating M_e has been checked[1] using an independent method based on viscosity measurements and found to be satisfactory.

Eventually, if one waits long enough, the entangled chains will slip past each other and the network will cease to exist. This gives rise to the additional elongation occurring beyond point C. Most of this additional elongation is also elastic in nature until ΔL becomes much larger than is indicated in the figure. It results from stretching of the chains as a whole rather than just those portions between initial entanglement points. However, at still later times, the chains having been elongated to an equilibrium value, additional elongation is the result of true viscous flow.
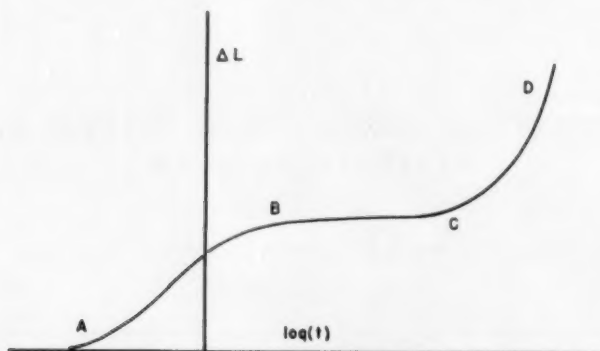
Fig. 1.—Typical creep curve for a very high molecular weight polymer.

The preceding statements presuppose a very high molecular weight polymer. For lower molecular weights the entanglements will unravel more easily and portion BC of the curve will become shorter. For $M \leqslant 20 M_e$ the plateau is essentially nonexistent. In that case, the true viscous flow also becomes dominant sooner.

For a typical rubber, one requires that the temperature be high enough so that point B is reached in a time of less than about 0.1 second. If such is not the case, the rubber will be too slow to be useful in any but slow deformation conditions. Ideally, too, the plateau region BC should be extremely long and flat.

Since it is impossible to obtain a suitably long plateau in practice, one introduces an artificial but stable network into the sample. By vulcanizing the polymer one hopes to replace the entanglement network by a permanent one. It appears that the success one has in achieving this aim is greater in the case of natural than for synthetic rubber. This is of primary concern when one considers hysteresis and heat build up effects in the rubber.

In order to see how the ideas outlined above fit into the problem of heat build up in rubber under repeated flexing, consider the rubber whose creep curve is shown in Figure 2. It will be shown in a later section that all rubbers measured conform to a curve of this general type at least to a first approxima-
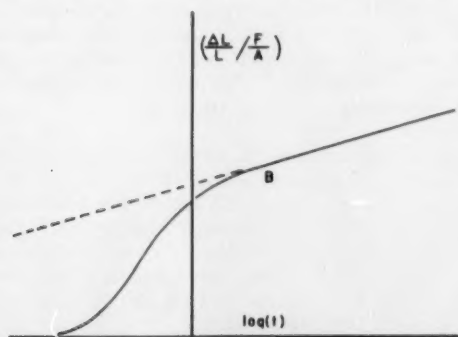
Fig. 2.—Typical creep curve for a vulcanized rubber.

tion. Under normal operating conditions for tires, the point B is reached in a time much shorter than the time taken for a tire to make one tenth of a revolution. If one approximates the load applied to the rubber in practice by a triangular force as shown in Figure 3, it is possible to compute the heat generated per unit volume of rubber per second. It turns out to be (see Appendix I):

$$\text{heat} = 6.6\kappa n F^2{}_{\max} \tag{1}$$

In this expression, κ is the slope of the long time portion of the curve in Figure 2, n is the frequency of the force impulses to the rubber, and $F_{\max}$ is the maximum tension experienced by the rubber. If a sinusoidal force had been assumed, the functional relationships of Equation (1) would not be changed although the numerical constant would be different.
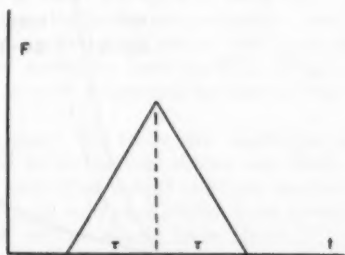
FIG. 3.—Applied force as a function of time used in obtaining Equation (1).

It is clear from Equation (1) that the primary factor governing heat generation in rubber under oscillatory tests is the flatness of the plateau in the curves of Figure 1 and 2. If the slope of the plateau, κ, is zero, the heat generated will be negligible. Similarly, a high slope gives rise to large quantities of heat being generated. In that which follows, it is shown that this factor is adequate to explain the excessive heat build up of SBR.

EXPERIMENTAL

Method.—The techniques used have been described in detail previously[1]. They consisted of applying a fixed load to the end of the sample and observing the elongation as a function of time. In this work the elongations were always kept below 5 per cent. The samples were maintained in a constant temperature chamber which regulated to approximately $0.2°$ C. Some difficulty was experienced as a result of crystallization in the natural rubber samples. This was minimized by taking readings immediately after lowering the temperature from about $40°$ C. Recovery as well as creep data were taken. Except in the most fluid polymers, the creep curve was reasonably reversible although small discrepancies may exist as found by Leaderman[2].

By making use of the equivalence of temperature and time it was possible to obtain a composite curve showing the tensile creep behavior of the sample over many decades of time. Each composite curve represents data taken at about ten temperatures. Since the curves will therefore have about 100 experimental points each, the actual points have not been included on the curves. The experimental error was small enough so that all the points lie quite accurately on the curves shown. All of the curves given in this report have been reduced to

10° C.   That is, the time scale is given for the rubber when held at 10° C.   By use of the shifting factors, a_T, given in a later section, one can convert the curves to other temperatures if desired.

Materials.—The polymers used in this study were furnished by The Good-year Tire and Rubber Company.   These samples were prepared from a single batch of each material so that the measurements would not be influenced by variations in raw polymer preparation.   The natural rubber was smoked sheet and the code numbers of the hot and cold SBR rubbers, unless otherwise stated, were GRS-1006 and 1500, respectively.
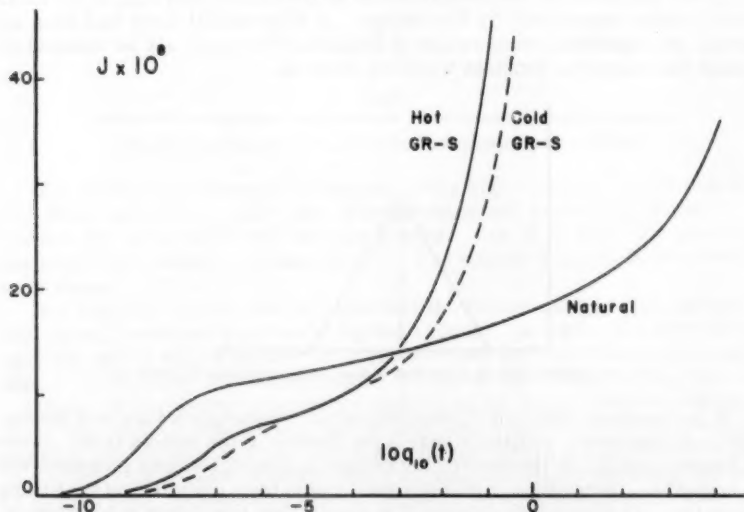
Fig. 4.—Tensile creep curves for pure, unmilled rubbers reduced to 10° C.   Compliance is in cm²/dyne and *t* is in minutes.

Preparation of the unvulcanized samples was usually carried out by evapor-ation of a chloroform solution of the polymer on a mercury surface.   The resulting films were dried under vacuum and eventually pressed together to form sheets about 1 mm thick.   The vulcanized samples and mixes were pre-pared according to the recipes given in Appendix II and were furnished to us in the form of sheets approximately 2 mm thick.

RESULTS

Unvulcanized raw rubbers.—The composite tensile creep curves at 10° C for the three uncompounded, unmilled basic rubbers are shown in Figure 4.   Be-cause of cumulative errors inherent in the superposition procedure, the error in the time scale may be as high as one-half decade.   (The creep compliance, J, plotted in Figure 4 is defined as $(\Delta L/L)/(F/A)$.)

Three features of interest should be pointed out about these curves.   First, the synthetic rubbers have a higher glass temperature than does natural rubber. This has been well known for several years and is of little consequence except for low temperature applications.

Second, the plateau for natural rubber is about twice as high as for synthetic. This feature was noticed previously by Zapas, Shufler, and DeWitt[3]. It is an indication of the tightness of the entanglement network in the polymer, SBR having the tighter network. One can use the familiar relation for network elasticity:

$$1/J = 3\nu\mathcal{K}T \tag{2}$$

to compute the molecular weight between entanglement points. It is found that M_e is approximately 4300 and 2200 for natural and SBR rubber, respectively. This corresponds to about 250 and 120 chain backbone atoms (Z_e) between the entanglement points. Since the average molecular weight per backbone atom is not too different for these two polymers, the total length of chain per unit volume is about the same in each case. Consequently major differences in entanglement behavior are probably a result of chain backbone flexibility. It is expected that stiff chains will have shorter entanglement lengths. One therefore concludes that the SBR chain is stiffer than that of natural rubber. This is not unexpected in view of the known structures of these chains.

For comparison purposes, the molecular weight per chain backbone atom will be taken as 17 and 18 for natural rubber and SBR, respectively. Since pure polystyrene has a molecular weight of 52 per backbone atom, one expects the total chain length in unit volume of rubber to be about 2.7 times larger than for polystyrene. Thus, rubber should have about 2.7 times more entanglements than polystyrene. Since Z_e for polystyrene is about 400[1], one would expect Z_e for rubber to be about 150 if the chains were comparable. Since Z_e for SBR is less than this, we would expect the SBR chain to be stiffer than polystyrene. On the same basis, natural rubber chains should be more flexible.

It will be seen in that which follows that this difference between natural and synthetic rubber is not of primary importance in respect to heat build up effects. It does, however, influence the modulus which one obtains at low degrees of crosslinking.

The third feature of interest about Figure 4 is the large difference in plateau lengths for natural and synthetic rubber. While the plateau for natural rubber is very long, that for the synthetics is so short as to be nearly nonexistent. At first thought one might think that crystallites in the natural rubber were retarding the slippage of the entanglement points. This view is disproved by the fact that much of the plateau region was measured at temperatures above 30° C, where no crystallinity should exist. In addition, the measurements of Zapas and others[3] on a much higher molecular weight SBR sample than used here, also show the long plateau evidenced here for natural rubber.

It is therefore concluded that the short plateau of the SBR samples is a reflection of the low molecular weight of the material. Current theory predicts[1] that the length of the plateau should vary approximately in proportion to $M_w^{4.4}$. Since it is doubtful that the values of M_w differ by as large a factor as Figure 4 would require, it must be concluded that the theory depends on a more sensitive molecular weight average than M_w or that the form of the theoretical relation is somewhat in error in this respect. In any event, it would appear that the low number-average molecular weight of SBR is responsible for the observed short plateau for this polymer.

Figure 4 also illustrates why SBR has extremely poor strength and elastic properties before vulcanization. At room temperature the rubber will show

considerable viscous flow even just a few seconds after an external load is applied.   It therefore shows considerable permanent deformation after the load is released.   In addition, the viscous flow decreases the effective number of chains holding the load on any given cross-section.   For this reason, the rubber is very weak under a slow test and, in fact, should have very nearly zero strength under an extremely slow test.   In contrast to this, natural rubber exhibits much less viscous flow at room temperature and will therefore show these bad effects to a much smaller degree.

Vulcanized rubbers without black.—Figures 5 and 6 show the creep curves for the unfilled but vulcanized polymers of Figure 4 in Formulation A as given in Appendix II.   The cures for the respective figures were 30 and 90 minutes at 200° F.   Other data for these polymers are given in Table I.   The curves for
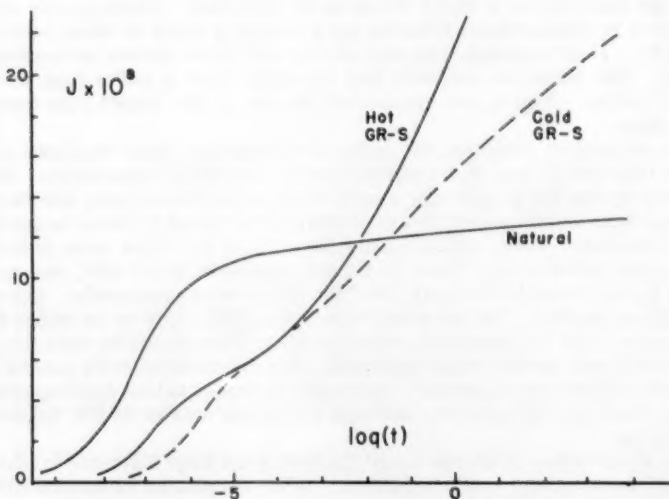
Fig. 5.—Tensile creep curves for unfilled rubbers vulcanized for 30 minutes at 290° F reduced to 10° C.   Compliance is in cm²/dyne and t is in minutes.

a 60-minute cure have also been obtained and they lie about midway between those for the two cures shown.   Striking differences are apparent between the effect of vulcanization on the natural and synthetic rubbers.

Apparently the vulcanization process has been very satisfactory in the case of natural rubber.   The primary molecules have been tied into a stable network which responds quickly under load and then remains at nearly constant elongation for long times thereafter.   Thus, the slope of the upper portion of the curve is near zero and, as outlined in a previous section, the vulcanized natural rubber should show relatively small heat build up.

Such is not the case for the SBR materials.   It is clear from Figures 5 and 6 that the molecules in this case have not been tied into a stable network.   As a result, the rubber never reaches an equilibrium extension under the applied load but, instead, continues to elongate indefinitely.   The consequent large slope, κ, of the long time portion of these curves results in large heat build up effects as shown in the theory section.   One could presumably vulcanize the rubber
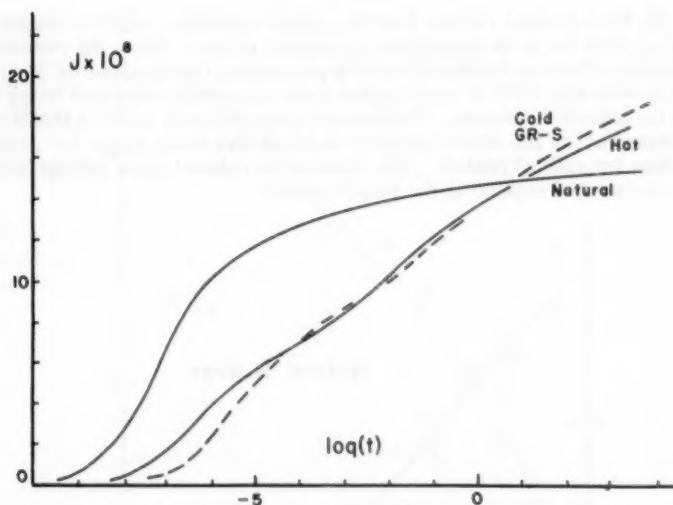
Fig. 6.—Tensile creep curves for unfilled rubbers vulcanized for 90 minutes at 290° F reduced to 10° C. Compliance is in cm²/dyne and t is in minutes.

more highly and, as a result, form a more stable network in the sample. However, it has been shown[4] that already the material is too highly crosslinked for optimum tensile strength and so higher degrees of crosslinking are not desirable.

Apparently the poor network formation in SBR is a result of the low number-average molecular weight of these materials. It will be recalled that, in forming a polymer network, one uses up as many crosslinks as one has primary molecules merely in joining the molecules together. These are essentially lost as far as network functions are concerned. Consequently, since SBR has a much lower M_n than does natural rubber, it is apparent that in order to obtain equivalent network structures one must go to much higher degrees of crosslinking in the case of SBR than would be necessary for natural rubber.

It would appear, then, that to make a more suitable synthetic rubber one should increase the molecular weight of SBR. This solution has the following drawback. SBR is known to have a much wider molecular weight distribution than does natural rubber. For this reason, the synthetic rubber not only has a

TABLE I

TENSILE STRENGTH DATA FOR MATERIALS OF FIGURES 5 AND 6

Compound	Cure, 290° F	Tensile strength, psi	Ultimate elongation, %	300% modulus, psi
Natural	30	2460	765	210
	60	2090	757	190
	120	1900	785	180
Hot SBR	30	200	815	75
	60	175	320	150
	120	175	290	—
Cold SBR	30	200	568	125
	60	180	600	110
	120	200	490	140

lower M_n than natural rubber, but the higher molecular weight averages, M_z and M_{z+1}, turn out to be larger than for natural rubber. Since the recoverable deformation of rubber during extrusion is proportional to the quantity $M_{z+1}M_z/M_w$, it is clear why SBR of much higher molecular weight than now being used would be difficult to process. Preliminary measurements made in this laboratory indicate that the above quantity is about five times larger for unmilled SBR than for natural rubber. The quantity is reduced upon milling because of the preferential rupture of the longer chains.

Natural Rubber

$loq_{10}(a_T)$

$10^3/T$
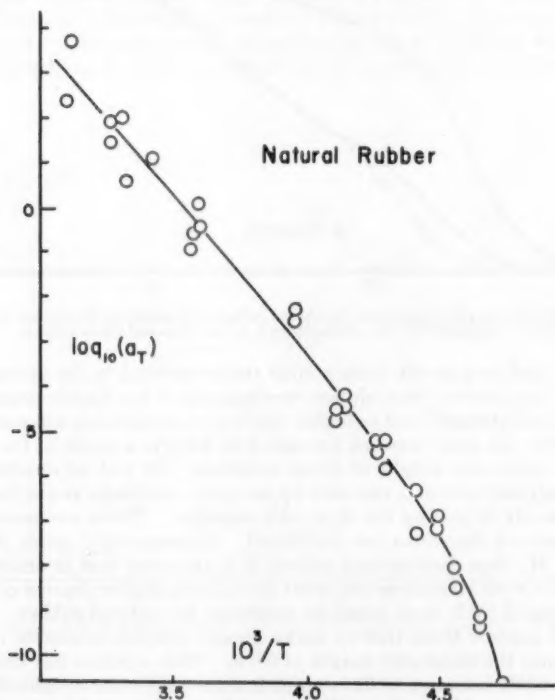
FIG. 7.—Superposition factors, a_T, for natural rubber.

As a by-product of the Ferry-Tobolsky temperature-time superposition procedure used in processing the data for Figures 4, 5, and 6, one obtains a set of shifting factors, a_T. These are defined in such a way that, if one wishes to obtain the time-dependence of the elongation at some temperature other than 10° C, say T, one merely considers the x axis to be a plot of log $(a_T t)$ rather than log (t). The values of these shifting factors are given in Figures 7, 8, and 9 for natural rubber and hot and cold SBR. It was found that ,to a fair approximation, the carbon black loaded rubbers conformed to these same values of a_T except at very low temperatures.

Loaded and vulcanized rubbers.—The properties of natural rubber and cold SBR containing various quantities of HAF carbon black in Formulation B are shown in Figures 10 through 12. In each graph the broken curves are for
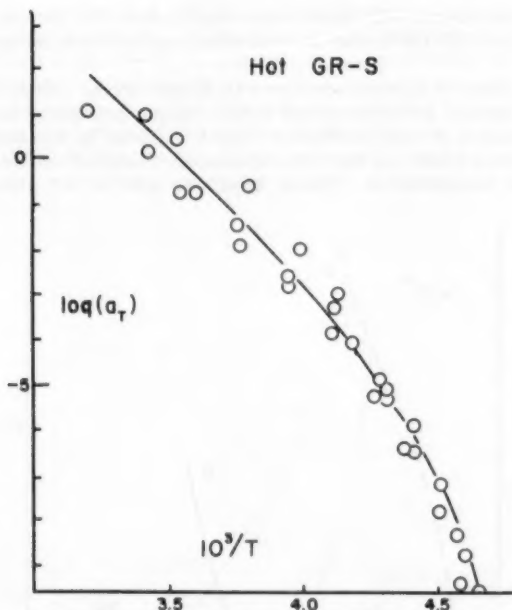
Fig. 8.—Superposition factors, a_T, for hot SBR.

natural rubber. Carbon black concentrations are given in each case on the basis of 100 parts by weight of the pure rubber. Similar data were obtained for hot SBR stocks but, since they differ only slightly from the cold SBR data, they are not shown here. It was found, however, that in the recipe used the
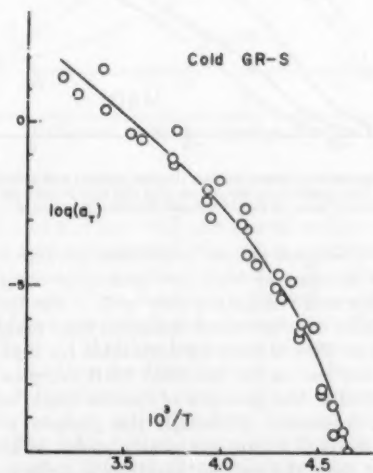
Fig. 9.—Superposition factors, a_T, for cold SBR.

hot SBR samples apparently cured more rapidly than did the cold rubber. A cure of 20 minutes for the former seemed about equivalent to 30 minutes for the latter.

Several features of interest are shown by these curves. First, it is apparent that the mechanical action involved in the milling procedure has greatly reduced the amount of high molecular weight material in the natural rubber. The long plateau found for the uncompounded, unmilled rubber is no longer present before vulcanization. From what was said in the previous section,
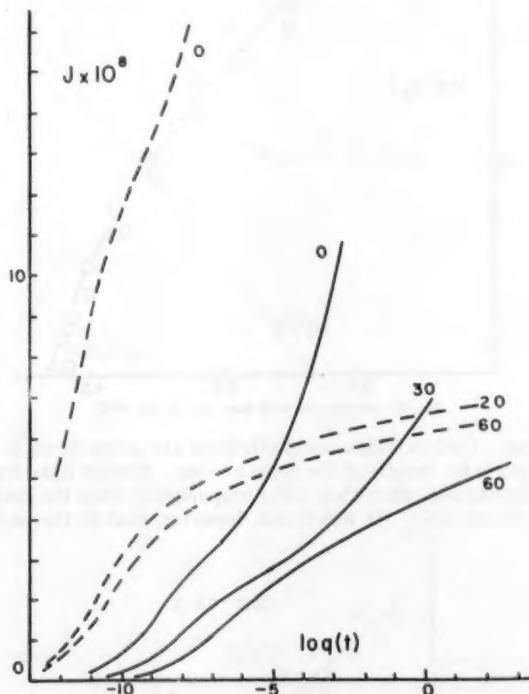
Fig. 10.—Tensile creep curves for natural rubber (broken curves) and cold SBR (full curves) containing 25 parts carbon black. The numbers on the curves give the cure in minutes at 280° F. All curves are reduced to 10° C, the compliance being in cm²/dyne and the time in minutes.

this indicates that the longest chains have been broken down. However, no great increase in the amount of very low molecular weight material has occurred since the rubber still vulcanizes very well. The less flat plateau in the case of the highest black concentration indicates that perhaps degradation has begun to decrease the facility of network formation for that formulation.

A comparison of the curves for the filled SBR samples with those given in Figures 5 and 6 shows that the presence of carbon black has resulted in a more satisfactory network response. Although the plateau portions of the SBR curves in Figures 10 through 12 are not nearly so flat as those for natural rubber, the improvement over the unfilled samples is quite obvious. As pointed

out in the "Theory" section, the slope of the plateau, κ, is proportional to the heat developed upon flexing. Since the curves do not correspond to the exact shape postulated in the theory, it is necessary to approximate the upper portion of the observed curve by a straight line. From a consideration of the frequency of flexing in tire applications and assuming an operating temperature of about 50° C, one can conclude that the portion of the curves up to about a 1-minute response at 10° C will be traced out under normal operating conditions. For this reason, we approximate the upper portions of the curves by the tangent line at log $(t) = 0$.
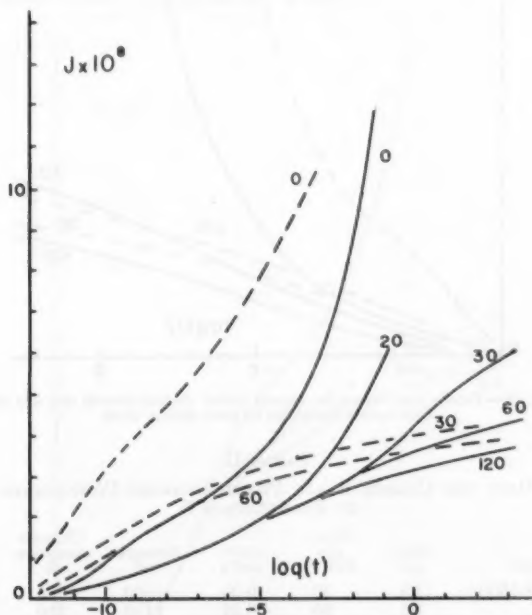
FIG. 11.—Tensile creep curves for natural rubber (broken curves) and cold SBR (full curves) containing 45 parts carbon black.

To the above approximation, one can compute the value of κ, proportional to the heat produced, for the materials studied. This has been done and the results for the filled cold and hot SBR samples as well as for natural rubber are given in Table II. For convenience, the other pertinent mechanical properties of these materials are also given in the table. No data for the unvulcanized and unfilled polymers are given there since the values of κ for these materials vary so widely that their interrelation is obvious from the graphs given.

It is seen from Table II that the heat evolved during flexing of natural rubber should be much less than for the synthetics. This is known to be true in practice and tends to confirm our considerations concerning heat build up. The differences between hot and cold SBR are not so obvious. One must examine the data in the table rather carefully before the reasons for the superiority of the cold rubber become clear. Comparison of the two rubbers at
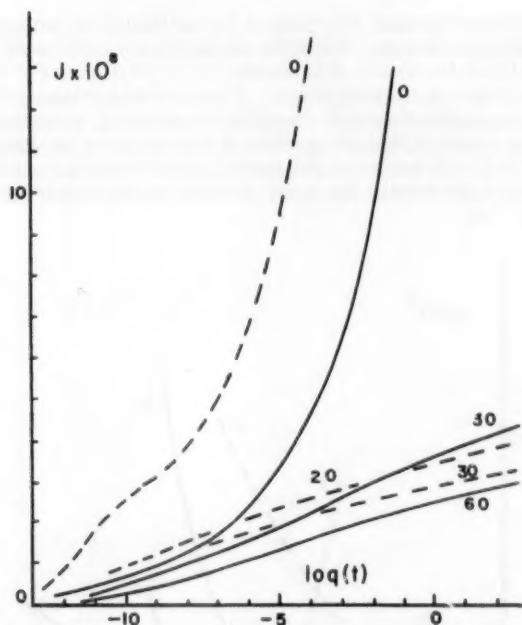
Fig. 12.—Tensile creep curves for natural rubber (broken curves) and cold SBR (full curves) containing 55 parts carbon black.

TABLE II

DATA FOR CARBON BLACK FILLED RUBBERS COMPOUNDED
IN FORMULATION B

Polymer	Black, phr	Cure, min 280° F	$\kappa \times 10^5$, cm³/g	Strength, psi	Ultimate elongation, %	300% modulus
C. GRS-1500	25	30	0.60	1560	645	300
	25	60	0.22	1110	310	1110
	45	30	0.42	2360	520	1000
	45	60	0.16	2225	300	2225
	45	120	0.12	1825	230	—
	55	30	0.20	2575	435	1500
	55	60	0.10	2750	280	—
H. GRS-1006	25	60	0.19	925	275	—
	45	20	0.41	1800	520	750
	45	30	0.21	2050	320	1850
	45	120	0.17	1860	225	—
	55	20	0.25	2400	465	1300
	55	60	0.12	2510	235	—
Natural	25	20	0.09	4355	620	1050
	25	60	0.07	3600	515	1200
	45	20	0.10	3925	450	2250
	45	30	0.09	3600	360	2900
	45	60	0.07	3400	345	3000
	55	20	0.12	3650	390	2750
	55	30	0.10	3600	360	2900

equivalent strengths and moduli shows that in each case the cold rubber will show less heat development. However, cold SBR would still appear to be definitely inferior to natural rubber in this respect.

As pointed out above, the larger heat generation of SBR is a result of its low number-average molecular weight, M_n. Apparently cold SBR has a some-what larger M_n than does hot SBR, thereby showing improved performance in this respect. Addition of carbon black to the rubber helps the rubber to form a more stable network than can exist without it. The process by which this occurs is still somewhat obscure. However, a study of Figures 10 through 12 gives some information concerning this matter.
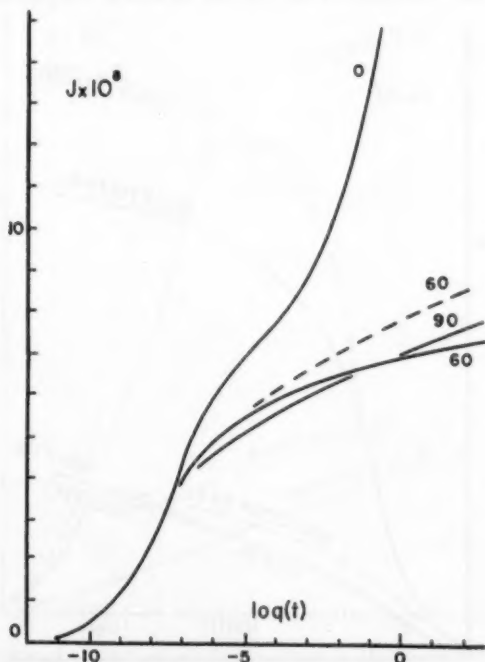
Fig. 13.—Creep curves for vulcanized high molecular weight cold SBR. The broken curve is for a polymer having a DSV of 2.92 while the polymer used for the other curves had a DSV of 3.37. Cures at 280° F are indicated on each curve. (Formulation B.)

It is apparent at once that the carbon black is relatively ineffective before vulcanization. The curves for the unvulcanized materials rise less steeply with increasing carbon black concentration. However, this is at least approximately what one would expect for the effect of solid particles added to any viscous liquid, polymeric or not. Our measurements were not extended far enough into the region of pure viscous flow to test this view with any precision. Certainly, however, the mere addition of carbon black has not led to any stable network within the polymer. One must conclude that, before the vulcanization takes place, no great number of chains can be attached permanently to the black.

After vulcanization the situation is somewhat different. The carbon black

obviously aids in forming a stable network. This has been known for many years and at least two ways for interpreting this behavior have been postulated. Guth and Gold[5] showed that rigid particles imbedded in an elastic rubber will tend to increase the modulus.

It is seen in Figures 10, 11, and 12 that the slight inflection in the curve for the unvulcanized natural rubber occurs at successively lower elongations for higher and higher carbon black concentration. If this is identified as the remnant of the plateau in the unmilled sample, then it would appear that this behavior is much like that predicted by Guth and Gold[5]. Unfortunately, the data of this report are not satisfactory for a quantitative comparison chiefly because of the poor definition of the plateau regions of the various curves.
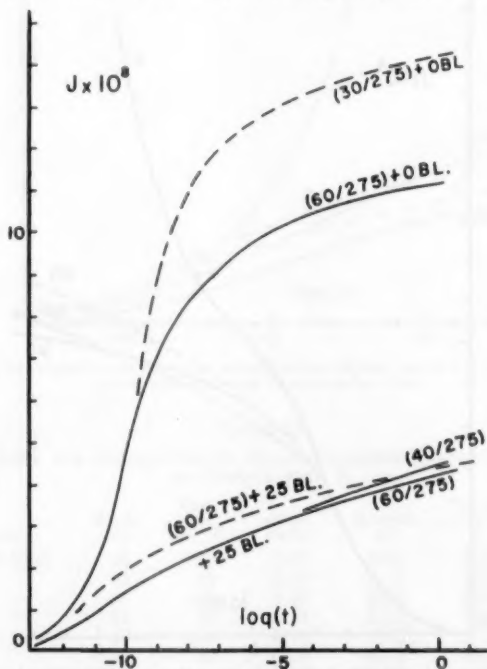
Fig. 14.—Creep curves for synthetic *cis*-polyisoprene with M_a = 157,000 (solid curves) compared to those for ordinary natural rubber (broken curves). The cures and black loadings are indicated on each curve.

An alternate view of the action of carbon black has been presented by A. M. Bueche[6]. He postulates that some of the rubber chains are attached to the black at various points. This action introduces additional crosslinks into the system and consequently the network is strengthened. The experimental data of this report conform to the general predictions of such a proposal also but once again the data neither prove nor disprove it.

It should be pointed out that previous tests of these theories may be only qualitative for the following reason. The creep curves for all of the filled rubbers examined in this work never show a completely horizontal plateau. This means that it is impossible to define a meaningful equilibrium modulus. Since both theories of reinforcement deal only with the modulus under equilibrium

conditions, it is clear that a definite test of them will encounter considerable difficulty. Apparently a fairly satisfactory test could be made using natural rubber but it is doubtful if comparison with the data for SBR can ever be anything but qualitative.

High molecular weight SBR.—Two cold rubbers used in making oil extended rubber have been studied. Their dilute solution viscosities (DSV) were 2.92 and 3.37. The data for the unfilled vulcanized polymers are shown in Figure 13. It is clear from a comparison with Figure 6 that these polymers are better in their vulcanization properties than is ordinary cold SBR.
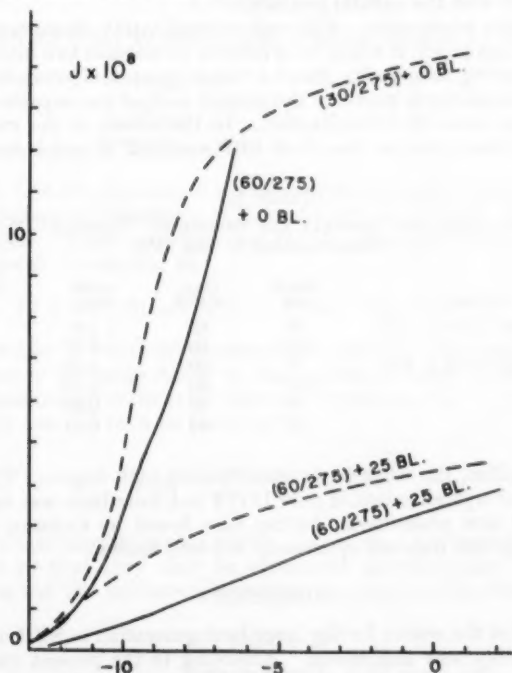
Fig. 15.—Creep curves for synthetic *cis*-polyisoprene with $M_n = 111,000$ (solid curves) as compared to those for ordinary natural rubber (broken curves). The cures and black loadings are indicated on each curve.

Considerable difference exists between the two polymers of Figure 13 also. As one would expect, the higher molecular weight polymer shows considerably better network formation. In fact, the 60-minute cure shows a behavior comparable to natural rubber. Although the addition of oil to this material before vulcanization will probably harm it to some extent, it is apparent that the low heat production found for this material in practice should not be unexpected.

Polybutadiene.—A sample of unfilled 122° F polybutadiene was also examined. It showed properties similar to ordinary hot SBR although its glass temperature was considerably lower than for SBR. The plateau region for this polymer was too poorly defined to obtain a precise estimate of its height.

Synthetic "natural" rubber.—Two synthetic *cis*-polyisoprenes with number-average molecular weights of 111,000 and 157,000 were measured. The data

for these are shown in Figures 14 and 15 together with that of a natural rubber control.   Physical data for these are given in Table III.

It is apparent that the 111,000 polymer is dangerously close to having an unacceptably low molecular weight.   Since ordinary SBR has an M_n not in excess of 110,000, it is obvious why it does not vulcanize acceptably.   The 157,000 polymer is clearly superior to the lower molecular weight one with respect to heat production properties, at least at low filler concentrations.   In addition, as seen in Table III, the strength of the low M polymer has been impaired by its low value of M_n.   The 157,000 polymer appears to compare reasonably well with the natural product.

Crystallization phenomena.—Although crystallization phenomena are not a logical part of this paper, it might be of interest to mention two interesting facts encountered during this work.   Since a small amount of crystallinity results in a rather large change in modulus, the present method was capable of detecting rather small amounts of crystallization.   In the course of the measurements we found that from time to time both SBR and 122° F polybutadiene would

TABLE III

COMPARATIVE DATA FOR NATURAL AND SYNTHETIC "NATURAL" RUBBER
(FORMULATIONS C AND D*)

Polymer	Black, phr	Cure, 275° F	$x \times 10^4$, cm³/g	Strength (approx.), psi
Synthetic (1.11 × 10⁵)	0	60	>1.0	130
	25*	60	0.17	2800
Synthetic (1.57 × 10⁵)	0	60	0.09	2900
	25*	60	0.12	3800
Natural	0	30	0.09	3700
	25*	60	0.11	3500

begin to crystallize, the latter to an unexpectedly high degree.   The optimum temperature for crystallization of pure 122° F polybutadiene was near −52° C. These are not new phenomena, having been found by Gehman and others[7] some years ago, but they are apparently not well known.

CONCLUSION

It is felt that the reason for the large heat generation in SBR under flexure is now reasonably well understood.   According to the present view, it is the result of the fact that M_n is too low in SBR thereby making it impossible to form a satisfactory network within the polymer.   When the molecular weight is increased, as is done with SBR used in oil extended polymers, a more suitable network is formed in the rubber during vulcanization and as a result this rubber shows less heat development.

Addition of carbon black to the rubber tends to increase the stability of the vulcanization network.   Whether this is a result of the purely mechanical effects of solid particles imbedded in the existing network or whether the black actually enters into the network structure through chemical bonding is still not clear.

In any event, it serves the function of retarding the creep of the polymer at long times.   The fact that the addition of black increases the generation of heat for the same *amplitude* of deformation is probably the result of the necessary increase in F_{max} needed to attain this deformation as predicted by Equation (1). The black's important function in regard to strength properties was discussed

briefly in a previous report[4] from this laboratory and will be investigated more in the future.

It should be pointed out that many of the observations and conclusions presented here have previously been presented by others although it is believed that now they will appear more logical and conclusive. Obviously it is impossible to mention all the pertinent work carried out in this field which has led others to conclusions similar to those presented here. Omission of such references was made necessary by the mere fact of their great number.

APPENDIX I

The applied force can be represented over one impulse by the equations:

$$F = (F_{max}/\tau)t \qquad 0 \leqslant t \leqslant \tau$$
$$= (F_{max}/\tau)[2\tau - t] \quad \tau \leqslant t \leqslant 2\tau$$
$$= 0 \text{ otherwise}$$

In order to find how the sample elongates with time under this applied force, we consider that small increments of force, $\Delta F/\Delta t$, are added to (or subtracted from) the sample. These values are just dF/dt. Each added force gives rise to a creep elongation represented by:

$$\Delta l = (dF/dt)_{t=\xi} \kappa \log [(t - \xi)/t_0] \quad \text{for } t > t_0 + \xi$$

where ξ is the time at which the increment of force was added and where $\log t_0$ is the intercept of the tangent line to the logarithmic creep curve. Summing all these elongations gives the total observed elongation, ΔL.

The energy loss will then be given by:

$$\text{Heat} = \int_0^\infty (d\Delta L/dt)F \, dt$$

where just a single impulse is considered. In practice, the impulses will be far enough apart so that they may be considered approximately independent. After carrying out the indicated operations, one obtains the result of Equation (1).

APPENDIX II

FORMULATION A

Rubber	100
Zinc oxide	3
Stearic acid	1.5
Sulfur	1.75[a]
Captax	0.75
Phenyl-2-naphthylamine	1.0

[a] 2.75 for natural rubber.

FORMULATION B

Rubber	100
Zinc oxide	3
Stearic acid	3[a]
Anax	1
Santocure	1.25[b]
Sulfur	2.0[c]

[a] 2.5 for natural rubber.
[b] 0.8 for natural rubber.
[c] 2.25 for natural rubber.

FORMULATION C

Rubber	100
Zinc oxide	6
Stearic acid	4
Sulfur	3
BLE	1
Captax	1[a]

[a] 1.25 when M_n = 111,000.

FORMULATION D

Rubber	100
Rosin acid softener	3
BLE	1
Stearic acid	2
Altax	0.8
Zinc oxide	3
Sulfur	2

SYNOPSIS

The tensile creep behavior of natural rubber, high and low temperature SBR, polybutadiene, and a synthetic cis-polyisoprene have been investigated. By combining measurements over the temperature range −70 to +60° C, it has been possible to obtain a composite creep curve covering over 15 decades of time for each of these materials. In addition, similar curves have been obtained for most of these materials at several degrees of cure and containing various amounts of carbon black. All measurements were confined to elongations below about 5 per cent. One can conclude from these data that the synthetic rubbers, except for the cis-polyisoprene, do not vulcanize to give a mechanically stable network. That is to say, these materials never reach equilibrium elongation under an applied load. It is concluded that the number-average molecular weights of SBR is so low that excessive degrees of crosslinking are needed in order to form a stable network. Natural rubber and certain synthetic cis-polyisoprenes do not suffer from this defect. The excessive heat generation found in SBR upon flexure is attributed to the fact that an equilibrium extension is never achieved in these materials. A theoretical relation for the heat production in flexed rubbers is given. It is shown that the theory predicts the relative behavior of the various rubbers in respect to heat generation under flexure.

ACKNOWLEDGMENT

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THE ULTIMATE PROPERTIES OF
SIMPLE ELASTOMERS *

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INTRODUCTION

The ultimate properties of polymers are very poorly understood. A large mass of practical data is available but at present there seem to be no molecular theories for its correlation or for use as a guide in obtaining new data[1].

In the following pages a theoretical approach to the ultimate properties of simple crosslinked elastomers will be described. The treatment will be limited to the tensile strength and ultimate elongation at temperatures high enough so that crystallinity and the viscous work during extension are negligible. The theory can be extended to cover compressive or shear strength with relatively little effort. The incorporation of the effects of viscosity and crystallinity will require somewhat more work. (After the completion of the major part of this work I learned that Prof. F. Bueche, University of Wyoming, has developed a somewhat similar theory for the tensile strength of *viscous* elastomers[2].)

A CRITERION FOR SAMPLE RUPTURE

The tensile testing of a sample is usually carried out by slowly increasing the length of the sample until rupture occurs. The retractive force and the relative elongation at the time of rupture are noted. We would like to find a useful criterion for this rupture point.

Consider a sample undergoing elongation. If at some time during this process the tension on one portion of the sample passes through a maximum, and continuously decreases after that time, this portion will elongate farther than the other parts of the sample. If during this time bonds are ruptured in the sample in such a way that it becomes easier to elongate and if the rate of bond rupture increases with increasing elongation the process may become catastrophic and lead to sample rupture.

We shall assume that the point of maximum tension, τ, defines the point at which rupture occurs and examine the consequences. This criterion for rupture can be written as:

$$(\partial \tau / \partial t)_c = 0 \tag{1}$$

where t denotes the time and the subscript c indicates that the portion of the sample is in this critical condition.

If the sample were perfect the entire sample might reach this critical condition simultaneously. In practice, however, it seems that no test sample can be made perfect. We would expect that the condition described by Equation (1) would exist in one region while other parts of the sample are not yet there. The region to reach this condition first will depend on the shape and degree of

perfection.   One would expect that a thin section or the edge of a cut or scratch would be under greater tension than the remainder of the sample.   These aspects will not be discussed any more in this treatment; we will assume here that such a region exists.

The evaluation of the consequences of our hypothesis requires that we have an expression for τ as a function of time.   Apparently no such general expression exists at present.   However, it seems safe to assume that the tension acting across a plane will be proportional to n, the number of bonds per unit area in the plane and to some function $\varphi(\alpha)$ describing the shape of the stress-strain curve.   Thus we will write:

$$\tau = Hn\varphi(\alpha) \tag{2}$$

where H is a proportionality constant and $\alpha = L/L_0$ where L and L_0 are the stretched and initial lengths of the sample.

Differentiating Equation (2) with respect to time and equating to zero, the criterion becomes:

$$-\left(\frac{1}{n}\frac{\partial n}{\partial t}\right)_c = \left(\frac{1}{\varphi}\frac{\partial \varphi}{\partial \alpha}\right)_c\left(\frac{\partial \alpha}{\partial t}\right)_c \tag{3}$$

where $(\partial\alpha/\partial t)_c$ is the critical rate of elongation.   In general the right side of Equation (3) can be determined from experiment.   The first factor can be determined from the shape of the stress-strain curve in the absence of the breaking of bonds.   In the case of simple elastomers at low rates of strain and high enough temperatures so that viscous and crystallinity effects are negligible $\varphi(\alpha)$ has been shown to be given to a good approximation by the kinetic theory result[1,3]

$$\varphi(\alpha) = \alpha - 1/\alpha^2 \tag{4}$$

In this case the work of extension per mole of chains between crosslinks becomes:

$$W = (RT/2)(\alpha^2 + 2\alpha^{-1} - 3) \tag{5}$$

These expressions of Equations (4) and (5) are reasonable approximations only at low extensions.   For higher values of α they have been found to give values that are too low.   In such cases the equations developed by Guth and James seem to represent the experimental values more precisely[1].

Since we either know or can determine the right side of Equation (3) the problem reduces to one of finding an expression for the rate of bond rupture in terms of the molecular constitution of the sample.   This will be attempted in the next section.

BOND RUPTURE IN DEFORMED ELASTOMERS

In the absence of a network or any applied force it might be expected that bonds would be broken according to the relation:

$$-(1/n)(\partial n/\partial t) = A \exp\{-\Delta F^{\ddagger}/RT\} \tag{6}$$

where the frequency factor is:

$$A = kT/h \tag{7}$$

and $\Delta F\ddagger$ is the free energy of activation for the process, R is the gas constant, T is the absolute temperature, k is Boltzmann's constant, and h is Planck's constant[4].

The formation of a network, a change in initial molecular weight of the polymer, and the deformation of the sample all change the free energy of the sample. If we are to compare samples having different degrees of crosslinking, and thus break at different elongations, we must choose our reference state so that it is independent of these conditions. It will be convenient in our case to take as the reference state that in which the bonds are contained in a noncrosslinked polymer molecule of very high molecular weight. When the sample is crosslinked and extended we will be increasing the free energy per mole of bonds by an amount ΔF. The rate of bond rupture is then:

$$- (1/n)(\partial n/\partial t) = A \exp\{- (\Delta F\ddagger/RT) + (\Delta F/RT)\} \tag{8}$$

The problem becomes one of finding an expression for ΔF.

To evaluate ΔF for our crosslinked deformed sample the following scheme is convenient. First we will find the expression for the disorientation entropy, S_1, per mole of bonds for the chains between crosslinks, treating them as being independent. We will subtract from this the disorientation entropy, S_0, per mole of bonds contained in chains of very high molecular weight. We will next find the change in configurational entropy, S_2, for crosslinking the chains using f-functional crosslinks. To this we will add the change of configurational entropy, S_3, on deformation. This, then, should be the total configurational entropy change per mole of bonds, ΔS, of forming the network from an original polymer of very high molecular weight. We will add a term representing the enthalpy changes during the crosslinking process.

Flory has shown that the disorientation entropy per mole of polymer chains, each chain having Z main chain bonds, is given to a good approximation by:

$$R\{\ln (Z) + ZG\} \tag{9}$$

where G is a constant depending on the flexibility of the polymer chain and where we have neglected unity compared to Z^1. For large Z the first term is small compared to the second so that dividing by Z we obtain:

$$S_0 = RG \tag{10}$$

Using Equation (9) we may write the configurational entropy per mole of bonds in our system of chains as:

$$S_1 = (R/Z) \ln (Z) + RG \tag{11}$$

The configurational entropy change upon connecting the ends of these ν moles of chains to f-functional crosslinks has been shown to be:

$$[2R\nu(f - 1)/f] \ln (2\nu N\Delta v/Ve) \tag{12}$$

where N is Avogadro's number and Δv is the small element of the total volume V in which f chain ends must exist if they are to take part in a single crosslink[5]. On the basis of a mole of bonds this becomes:

$$S_2 = [2R(f - 1)/Zf] \ln (2\nu N\Delta v/Ve) \tag{13}$$

The quantity in the logarithmic factor may be simplified by realizing that Δv is the volume of approximately f bonds, i.e., $\Delta v \cong fv_0/N$, where v_0 is the molar volume of the bonds. In making this substitution and using the relations $n = \nu Z$ and $nv_0 = V$, Equation (13) becomes:

$$S_2 = [2R(f - 1)/Zf] \ln (2f/Ze) \qquad (14)$$

The entropy change during deformation is according to Equation (5) or a modification thereof:

$$S_3 = - W/TZ \qquad (15)$$

The crosslinking process will be accompanied by an enthalpy change in addition to the entropy changes described above. The magnitude of this change is expected to depend on the type of crosslinks formed. The change in crosslinking a hydrocarbon chain, for instance, might be estimated from the bond energies of the two carbon-hydrogen bonds broken and the new carbon-carbon bonds formed during the crosslinking process. This would correspond to an increase in enthalpy per mole of crosslinks of approximately 114 kcal. It is to be expected that such an estimate, based on reported bond energies, will be rather rough. It should, however, give the order of magnitude to be expected. For the present purposes we will not try to be more explicit. The parameter ΔH, representing the enthalpy change of the polymer sample during formation of a mole of chains between crosslinks, will be introduced. The change per mole of bonds becomes $\Delta H/Z$. The total free energy change becomes then:

$$\Delta F = \frac{\Delta H}{Z} - T(S_3 + S_2 + S_1 - S_0)$$
$$= \frac{\Delta H}{Z} + \frac{RT}{Z} \left\{ \frac{W}{RT} - \left[\frac{2(f - 1)}{f} \right] \ln \left(\frac{2f}{Ze} \right) - \text{nl } Z \right\} \qquad (16)$$

If our crosslinks are tetrafunctional this becomes:

$$\Delta F = \frac{\Delta H}{Z} + \frac{RT}{Z} \left\{ \frac{W}{RT} + \left(\frac{1}{2} \right) \ln (Z) - \left(\frac{3}{2} \right) \ln \left(\frac{8}{e} \right) \right\} \qquad (17)$$

The rate may now be obtained by substituting for ΔF in Equation (8).

For comparison with experiment we will have to know how to express Z in terms of measurable quantities. If all but a negligible number of the bonds in the sample are in the chains between crosslinks and if we remember that v_0 is the volume of one mole of bonds we can write:

$$Z = \frac{1}{v_0} (V/\nu) \qquad (18)$$

The quantity (ν/V) may be determined from the equilibrium tension at a given elongation by the use of the kinetic theory result:

$$\tau = RT(\nu/V) \, \varphi(\alpha) \qquad (19)$$

or from a detailed knowledge of the chemical constitution of the sample.

When the degree of crosslinking is low or if the initial polymer, before cross-linking, had a low molecular weight the fraction of the bonds in the sample that are not in chains between crosslinks may be appreciable[1]. In such cases a correction must be made in the value of Z determined by Equation (18). Flory has shown that the fraction of bonds that are in chains between crosslinks is given approximately by:

$$S_a = \nu/(\nu + 2N) \tag{20}$$

Making the substitutions:

$$\nu/V = 2(C - \rho/M)$$

and $N/V = \rho/M$ where C is the number of moles of crosslinks per unit volume of the sample, ρ is the polymer density, and M is the initial molecular weight we have that:

$$S_a = (C - \rho/M)C \tag{21}$$

When this correction is important the true value of Z will be that given by Equation (18) multiplied by S_a.

The criterion for rupture can now be written as:

$$\left(\frac{1}{\varphi}\frac{\partial\varphi}{\partial\alpha}\right)_e \left(\frac{\partial\alpha}{\partial t}\right)_e$$
$$= A \exp\left\{-\left(\frac{\Delta F\ddagger}{RT}\right) + \frac{1}{Z}\left[\frac{W_c}{RT} + \frac{1}{2}\ln(Z) - \frac{3}{2}\ln\left(\frac{8}{e}\right) + \frac{\Delta H}{RT}\right]\right\} \tag{22}$$

This can be put into a more convenient form for comparison with experiment by taking logarithms of both sides and rearranging so that:

$$\frac{W_c}{RT} - Z\ln\left(\frac{1}{\varphi}\frac{\partial\varphi}{\partial\alpha}\right)_e + \frac{1}{2}\ln Z - \frac{3}{2}\ln\left(\frac{8}{e}\right) = BZ - \frac{\Delta H}{RT} = Y \tag{23}$$

where:

$$B = \frac{\Delta F\ddagger}{RT} + \ln\left(\frac{\partial\alpha}{\partial t}\right)_e - \ln(A) \tag{24}$$

Thus a plot of the measured quantities on the left side of Equation (23) vs Z should be linear and have a slope B. If the rate of elongation is known the free energy of activation can be calculated from the value of B determined in this way. The intercept at $Z = 0$ determines the value of $\Delta H/RT$.

An examination of the negative rate of chain rupture as given by the right side of Equation (22) indicates that bonds may be broken in a sample even though it is not deformed, i.e., W is zero. It appears that difficulty would be encountered, in some cases, in producing a highly crosslinked sample even though a linear molecule of high molecular weight might be quite stable. In this case it might be expected that the polymer would tend to take up other configurations, such as rings, etc., which would not result in effective crosslinks, if such configurations were possible.

The quantity $(1/\varphi)(\partial\varphi/\partial\alpha)$ decreases as α increases when $\varphi(\alpha)$ is given by

Equation (4) or by expressions describing Hookian behavior. It might be expected, then, that as the activation energy $\Delta F^{\ddagger}$ decreases the elongation at break, α_c would also decrease. The value of α_c, according to the present hypothesis, should also increase as the rate at which the sample is tested increases. For normal tensile tests this dependence should be slight but may be appreciable for very fast ones.

In principle the time necessary for breaking a sample could be obtained by integrating Equation (8) to find the time necessary to break a major fraction of the bonds. This integration appears to be rather involved and will not be carried out at this time.

In obtaining Equation (23) average values of Z and W_c have been used. An actual sample will have a distribution of lengths of chains between crosslinks and a distribution of energies of these chains. Approximate calculations have indicated that consideration of these effects will not change the form of Equation (23) appreciably except for low values of Z. These calculations will not be described here.

TABLE I

ULTIMATE PROPERTIES OF A CROSSLINKED POLYDIMETHYLSILOXANE

Dose, MR^a	τ_c (kg/cm²)	α_c	Z	W_c/RT
5	4.35	4	270	6.75
10	4.48	2.4	143	1.78
20	4.23	1.6	101	.41
50	3.73	1.1–1.2	53	~.09

ᵃ MR stands for millions of equivalent roentgen units as determined by an air ionization chamber.

The rupture of a polymer sample requires that more surface be formed. A consideration of this requirement leads to the conclusion that the sample cannot be ruptured unless it contains at least enough energy to form this new surface. Since for elastomers, as normally tested, this energy is expected to be low the effect will be neglected. Because of this, however, the derived relationships will be expected to fail at very low rates of test and low elongations, i.e., some samples can never rupture, no matter how slow the test, until enough energy has been stored to create the new surface.

CONFRONTATION WITH EXPERIMENT

In some preliminary experiments, which we plan to continue, a linear polydimethylsiloxane having an intrinsic viscosity of $[\eta] = 136$ cc/gram in toluene at 25° C was crosslinked using high energy electrons. The samples were found to have completely reversible stress-strain curves at room temperature even at elongations close to the ultimate elongation. Elongated samples showed no measurable stress relaxation over periods as long as three days. This was taken as evidence for the absence of a significant amount of chemical stress relaxation.

Dumbbell shaped samples at about 26° C were stretched in a tensile testing machine until they broke. The rate of elongation was 0.25 per minute. This rate was small enough so that when the elongation process was stopped before the sample ruptured no measurable viscous type relaxation was observed. The elongation, α_c, and tension τ_c, at break are recorded in Table I.

Values of Z were computed from the equilibrium tensions at low elongations using Equations (18) and (19) by using values of $v_0 = 74$ cc per mole and $RT = 600$ cal/mole. Use of the tensions at low elongations in this computa-

tion seemed to be more reliable since the stress-strain curves deviated somewhat from the form of $\varphi(\alpha)$ at high elongations. Had the values of τ_c been used, the magnitude of these deviations would have changed from sample to sample as α_e varied. It is difficult to decide whether or not v_0 should have been taken as one half the above value. Fortunately the final results are very insensitive to this change in v_0. Since the lowest radiation dose for the samples measured was at least 20 times the dose necessary for gelation, the correction of the Z values by use of Equation (21) was not necessary. The values of W_c/RT, computed from the measured α_e's using Equation (5), are also shown in Table I. Values of Y are computed as indicated by Equation (23) and are plotted as a function of Z in Figure 1.
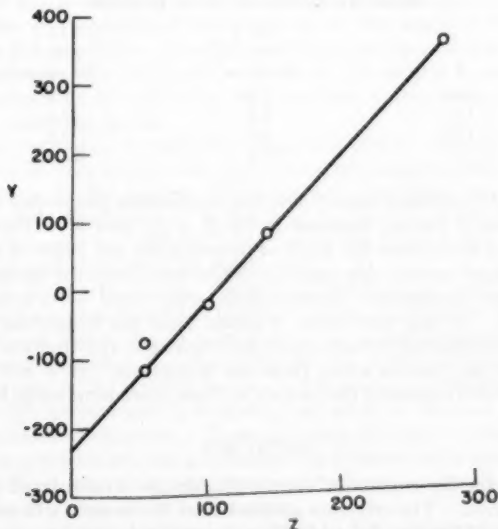
Fig. 1.—Ultimate elongation data plotted as suggested by Equation (23). Each point is the average of three determinations.

Within the limits of error of the experiments all the points fall on a straight line having a slope $B = 2.3$. The intercept of the line at $Z = 1$ is -235. If we take $A = 10^{13}$ per sec and $(\partial\alpha/\partial t)_c = 4 \times 10^{-3}$ per sec this value of B leads to $(\Delta F\ddagger/RT) = 37.8$, which is equivalent to $\Delta F\ddagger = 22.6$ kcal per mole. It is interesting to compare the value with the activation energy found by stress relaxation measurements at different temperatures on a similar polymer[6]. The value found in that case was 22.8 kcal per mole. Since the two are not expected to be exactly the same, this would seem to be reasonable agreement[4].

The value of ΔH determined using the intercept at $Z = 0$ is 141 kcal per mole of chains between crosslinks. Since in a tetrafunctionally crosslinked system each crosslink results in two chains the value per mole of crosslinks is twice the above number. Based on the previous estimate this seems to be too high by a factor of two. If the chemical details of the crosslinking of polydimethylsiloxanes by electron irradiation were known we might be in a better position to discuss the significance of this value.

Having determined the values of the parameters $\Delta F^{\ddagger}$ and ΔH from Figure 1 it is now possible to compare the rates. The criterion for rupture required that Equation (3) hold. The rates have been computed using the data of Table I and Equations (4), (8), and (17). They are recorded in Table II. The agreement seems to be within the limits of experimental error. The rates computed using $\varphi(\alpha)$ are very sensitive to small changes of α_c for low elongations. A variation of α_c from 1.1 to 1.2 is responsible for the difference in the tabulated values for the case $Z = 53$. Future experiments might be directed toward obtaining more accurate values in this region.

TABLE II
RELATIVE RATES OF BOND RUPTURE

Z	$\left(-\dfrac{1}{n}\dfrac{\partial n}{\partial t}\right)_s \times$ 10^3 per sec	$\left(\dfrac{1}{\varphi}\dfrac{\partial \varphi}{\partial t}\right)_s \times$ 10^3 per sec
270	1.0	1.0
143	2.2	2.0
101	4.1	4.8
53	32.7	37–17

The present treatment introduces the equilibrium properties of the system for the purposes of finding expressions for Z, $\varphi(\alpha)$, and W. The quantities Z and W are used to express the work of deformation per network bond. For a highly crosslinked sample this could be determined from the stress-strain curve and the sample dimensions. Presumably, $\varphi(\alpha)$ could be determined by the same methods. If this were done it seems that the restriction of negligible viscosity and crystallinity effects could be eliminated and that the above analysis might apply to systems where these are important. How well the relations presented here will represent the factors in those cases remains to be determined by experiment.

SYNOPSIS

A criterion for the rupture of simple elastomers is postulated and its consequences examined. The criterion assumes that the sample will break when the rate of increase of tension due to further elongation is equal to the decrease due to bond rupture. The former is computed from the rate of strain and the form of the stress-strain curve. An expression for the latter is found using reaction rate considerations. The resulting expressions represent the experimental data on the rupture of polydimethylsiloxanes within the limits of experimental error. The free energy of activation for bond rupture obtained from the tensile data, by use of the theory, at one temperature is in approximate agreement with the activation energy obtained from stress relaxation measurements at several temperatures.

ACKNOWLEDGMENT

I am indebted to A. V. White and J. S. Balwit for making the preliminary measurements.

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INFLUENCE OF MOLECULAR SHAPE ON THE TENSILE STRENGTH OF VULCANIZATES *

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A study of the mechanism of the formation of albuminous gels[1] has shown that the mechanical strength of films depends on the shape of the chain molecules. Films prepared from globular casein have a lower tensile strength than those prepared from fibrillar casein[2]. It would be natural to assume that the mechanical properties of rubberlike polymers and vulcanizates depend on the shape of the molecular chains.

In order to verify this hypothesis, vulcanized films[3] prepared from solutions of butyl rubber in various solvents were examined, assuming that the degree of twisting depends on the nature of the solvent. Benzene and carbon tetrachloride, in which the degree of twisting of the butyl rubber chains is quite different, were chosen as solvents. The tensile strengths given in Table I are the mean statistical data from 25 specimens.

Data of the change in relative viscosity of solutions of butyl rubber in benzene and in carbon tetrachloride as functions of the temperature and concentration are shown in Figure 1. It is seen that the relative viscosity of benzene solutions is lower than that of carbon tetrachloride solutions of equal concentration. An increase in the relative viscosity of benzene solutions of butyl rubber is observed with an increase in temperature, while a decrease is observed in carbon tetrachloride solutions. These changes of relative viscosity with an increase in temperature are less pronounced in solutions with concentrations up to 0.3 g per 100 cc, where the polymer forms true molecular solutions, and are more pronounced in concentrated solutions.

Several investigators[4] obtained similar data for polyisobutylene; solutions of the latter in a thermodynamically "weak" solvent had a positive temperature coefficient of change of relative viscosity, and in a "good" solvent, a negative coefficient.

It is natural to ascribe the increase in relative viscosity of benzene solutions of butyl rubber during heating to the uncoiling of the twisted molecular knots and the decrease in the relative viscosity of carbon tetrachloride solutions to the twisting of the relatively straight polymer chains into denser knots. The gelation of benzene solutions of butyl rubber during heating also reflects this twisting of the chains.

When the temperature of benzene solutions of butyl rubber of concentration greater than 3 g per 100 cc rises to 80°, a swollen gel is precipitated; if the temperature is reduced, the gel again dissolves. The formation of a gel under these conditions can be due only to untwisting of the molecular knots and consequent increase of molecular reactions between the chains. No gel formation is observed even when solutions of concentrations of 5 to 10 g per 100 cc are heated in carbon tetrachloride.

TABLE I

		Benzene			Carbon tetrachloride	
		Tensile strength, kg/sq cm		Relative elongation, %	Tensile strength, kg/sq cm		Relative elongation, %
Time of vulcanization, min		Calculated for			Calculated for		
		Initial cross-section	Actual cross-section		Initial cross-section	Actual cross-section	
A	70	49.5	288	482	110.5	852	671
	100	46.1	278	501	112	888	692
	120	43.9	264	504	107	819	665
B	70	90.6	806	794	87.4	786	799
	100	75.7	662	774	76.5	624	717

Experimental data for both types of vulcanizates are given in Table IA, showing that those prepared from carbon tetrachloride have a tensile strength almost three times that of vulcanizates from benzene solutions.

Consequently two fundamental conclusions can be made; i.e., (1) the original shape of the chains, which is governed by the nature of the solvent, is determined on the surface of the carbon black particles and is preserved during vulcanization, and (2) vulcanizates with relatively straight chains have greater tensile strength than those with twisted chains.

The higher mechanical strength of vulcanizates prepared from carbon tetrachloride solutions may be due to the greater intermolecular activity between the straight chains and between the polymer and the carbon black particles.

This reinforcement of rubbers by carbon blacks is governed to a large degree by the orientation of the straight chains on the surface of the carbon black particles and the ensuing increased intermolecular reaction between the polymer chains and between the polymer and the carbon black particles.
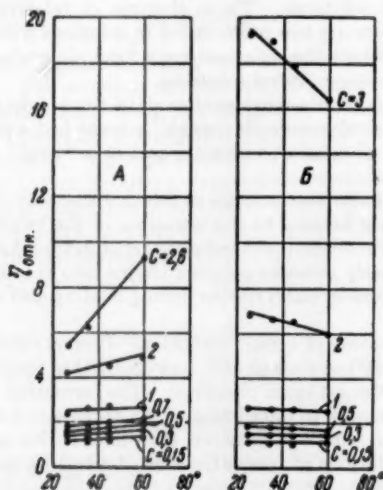
FIG. 1.—Variation in the relative viscosity of solutions of butyl rubber in benzene (A) and carbon tetrachloride (B) as a function of concentration and temperature.

Further evidence in support of this conclusion are the experiments on vulcanization of deformed films prepared according to the same recipe from benzene and carbon tetrachloride solutions. Before vulcanization the films were stretched 100 per cent in a special apparatus and vulcanized just as in the first experiment. Data on the mechanical properties of films vulcanized in the deformed state are shown in Table IB. These data show that, when stretched films prepared from benzene solutions are vulcanized, the tensile strength increases to a point corresponding to that of films from carbon tetrachloride solutions vulcanized in the relaxed state. The tensile strength of films from carbon tetrachloride solutions vulcanized in the deformed state is almost constant in comparison with films vulcanized in the relaxed state.

From this it follows that when unvulcanized films from benzene solutions are stretched, the chains are straightened and oriented: the same process of twisting and formation of straight chains which takes place in films from carbon tetrachloride solutions.

Thus, the experimental data show that the original shape of the polymer chains which form the spatial network is one of the chief factors which govern the tensile strength of vulcanizates.

The data and conclusions presented in this article show a means for improving both the mechanical properties of vulcanizates and the choice of plasticizers. In particular, these results can be used to obtain vulcanized films of greater strength in the manufacture of rubber goods from solutions by the use of a "good" solvent.

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[3] The composition of the mixture was the following (parts by weight): butyl rubber, 100; stearic acid, 3; zinc oxide, 5; magnesium oxide, 20; thiuram, 1.3; mercaptobenzothiazole, 0.65; lampblack, 40; sulfur, 2.0. The films were vulcanized at 143° in nitrogen, and their mechanical properties were measured on a dynamometer with the lower clamp moving at a rate of 500 mm/min. The specimens were ring-shaped, 15–20 mm in diameter, 0.2–0.3 mm thick, and 3.4 mm wide.

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SKI RUBBER, POLYISOPRENE, SIMILAR TO NATURAL RUBBER *

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B. K. Karmin, L. S. Priss, M. M. Reznikovskiy, L. A. Chernikina,
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Years of research at the S. V. Lebedev All-Union Scientific Research Institute for Synthetic Rubber[1,2] have provided industry with a number of methods for making synthetic rubber from isoprene. Of all the known synthetic rubbers this comes closest to natural rubber in structure and properties; it is the best available substitute of natural rubber, possessing a high degree of elasticity and strength.

The present article is a brief summary of the basic work on isoprene rubber done by the Scientific Research Institute of the Tire Industry. On the basis of this work recommendations were made for the development of the production of synthetic isoprene rubber and the substitution of isoprene rubber for natural rubber in the manufacture of heavy duty truck tires.

By using different polymerization processes it is possible to produce isoprene rubbers whose chain structures are very similar, but whose molecular weights, and therefore physical and technological properties, are very different. The *cis* structure of the 1,4 polyisoprene chains is the basic structural element of the new isoprene polymer. Therefore these synthetic isoprene rubbers (SKI) obtained through catalytic polymerization when vulcanized show a crystalline structure when x-rayed in the stretched state. The x-ray photographs also show that the geometric distribution of interference spots in SKI rubbers corresponds to the distribution of interference spots in natural rubber, but that the relative intensities of the crystalline, liquid, and amorphous scatterings in the two rubbers are different (Figure 1).

The intensity and size of the crystalline interference spots (other factors such as temperature, magnitude, and duration of deformation being equal) depend not only on the relative amounts of *cis* links in the 1,4 structure and other structures, but also on the extent of chain branching and the density and homogeneity of the molecular lattices in the vulcanizate.

A fairly close approximation to the structure of natural rubber (98–100 per cent of *cis* links in the 1,4 structure) may be achieved by directing the catalytic chain polymerization of isoprene in a particular way; this is shown by the gradual increase in the similarity of all parameters in x-ray photographs of SKI and NR (natural) rubbers.

A study of the plastic and elastic properties of raw (unvulcanized) SKI samples, with different mean molecular weights, shows that SKI is closer to masticated natural rubber in its ratio of plasticity to recovery (Figure 2), but that its recovery is less than that of other synthetic rubbers.

When for technical reasons SKI rubbers are polymerized to produce high molecular weight mixtures, too stiff for the formation of technologically desirable mixtures, the necessary plasticity may be achieved in several ways: (1) masti-
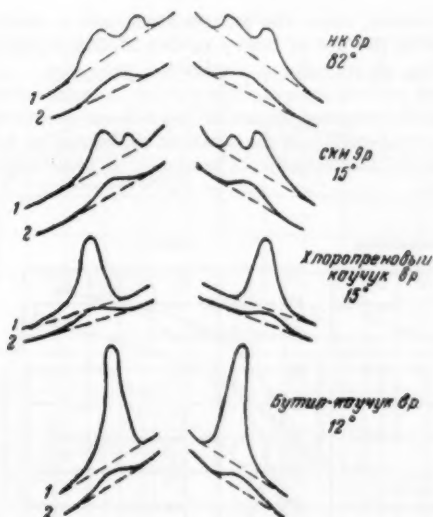
FIG. 1.—Photometric curves made from x-ray photographs of SKI, NR, chloroprene and butyl rubbers. *1*—Intensity of film darkening along the line of crystalline interferences. *2*—The same, along the line of the amorphous halo 6, 8, 9—samples stretched, respectively, 6, 8, and 9 times their length. 12°, 15°, 82° C —temperature of samples at which x-ray photographs were taken.

cation on cold rolls, (2) mastication in closed mixers, (3) thermal oxidation in kettles (Figures 3 and 4), (4) the addition of low molecular weight polyisoprene fractions, and (5) the addition of various softeners.

The tire and rubber industry is particularly interested in rubbers which do
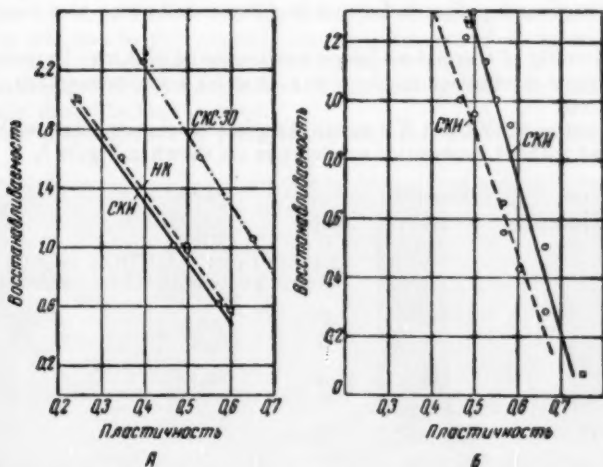
FIG. 2.—Comparison of plasticity and recovery (in meters) of crude and masticated rubbers. The ordinate is recovery and abscissa plasticity. A—SKI, NR, and SKS-30A rubbers. B—SKN masticated rubber obtained by treatment on rolls (- - -); by thermal oxidation (—).

not require mastication, since the process consumes a great amount of time and energy, involves the use of heavy rubber mixing equipment, and creates difficulties in setting up continuous production processes.

When SKI. just as butadiene-styrene rubber, is masticated mechanically at low temperatures, the resulting material has a lower recovery than when it is obtained with thermal-oxidation mastication conducted in kettles and rubber mixers (see Figure 2); this indicates a tendency in these rubbers to recombine and form structure.
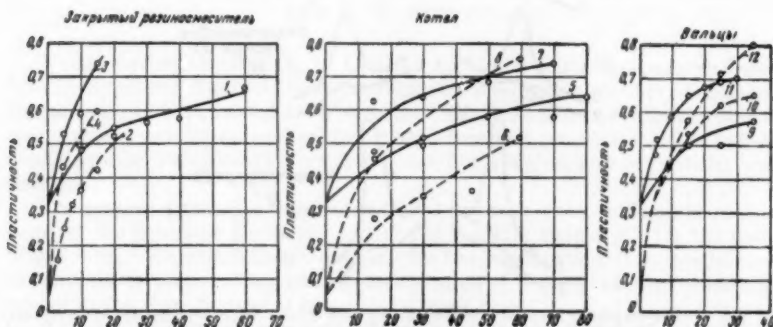
Fig. 3.—The kinetics of SKI mastication on rolls and the kinetics of thermal oxidation in a kettle and in a closed rubber mixer with MBTS and without an accelerator.   Ordinate is plasticity and abscissa mastication time in minutes.

The greater the number of 1,2 and 3,4 structure links in the molecular chains, the greater the intensity of the processes just described.

At about 140° C and with an insufficiency of oxygen in the system, the reactions of recombination and structure formation develop to a considerable degree.

The intensity of thermal-oxidation mastication of SKI may be increased by adding various mastication accelerators such as fat acids, mercaptans, phenols, disulfides, etc.

The kinetics of SKI and NR mastication in a laboratory mixer with MBTS (Altax) and without mastication accelerators are shown in Figure 3.

Apparatus	Temp., ° C	Rubber	Curve
Closed rubber mixer	140°	SKI	1
		NR	2
		SKI with 1 part of MBTS by weight	3
		NR with 1 part of MBTS by weight	4
Kettle	135°	SKI	5
		NR	6
	145°	SKI	7
		NR	8
Rolls	20°–80°	SKI	9
		NR	10
		SKI	11
		NR	12
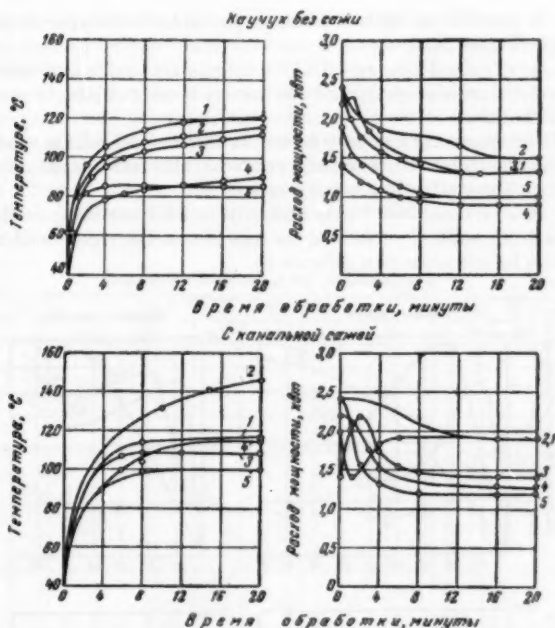
Fig. 4.—Rise in temperature during the treatment of SKI in a rubber mixer, with and without carbon black, and the consumption of energy during these processes (rate of mixer roll rotation is 53–63 rev/min) Ordinate is temperature, ° C, and abscissa is duration of treatment in minutes.

The slow rise in temperature is due to the low internal friction of SKI rubbers, and is indicated by the comparatively small amount of energy required to carry out the above described processes (Figure 4).

In planning procedures for mixing and masticating SKI in rubber mixers these factors should be kept in mind.

With the proper degree of plasticity in SKI and the correct selection of
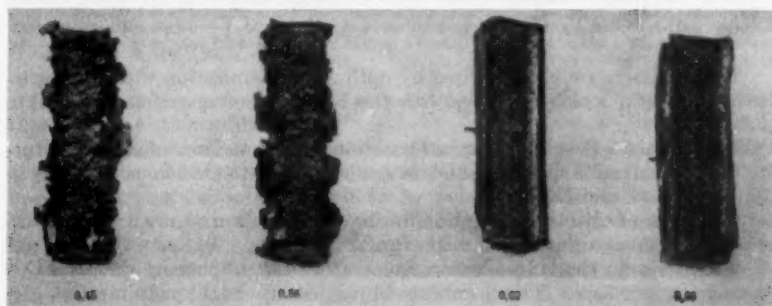
Fig. 5.—Photographs of extruded samples of tread rubbers made from masticated SKI rubbers of 0.45, 0.56, 0.62 and 0.68 plasticity, containing 50 parts of channel black by weight.

softeners it is possible to obtain tread type rubber mixtures of satisfactory extrudability (Figure 5).

The process of calendering raw SKI containing zinc oxide and various carbon blacks (channel, furnace, etc.), and the use of these rubbers in coating cord, creates no difficulties.

Raw SKI mixtures are not very tacky; in this respect SKI is similar to synthetic rubber, and differs from natural rubber (NR) and the chloroprene polymers which, on the contrary, are very tacky.

Unfilled and carbon-filled vulcanizates from SKI are very similar to their counterparts from natural rubber in the kinetics of the changes in mechanical properties due to vulcanization (Figure 6).
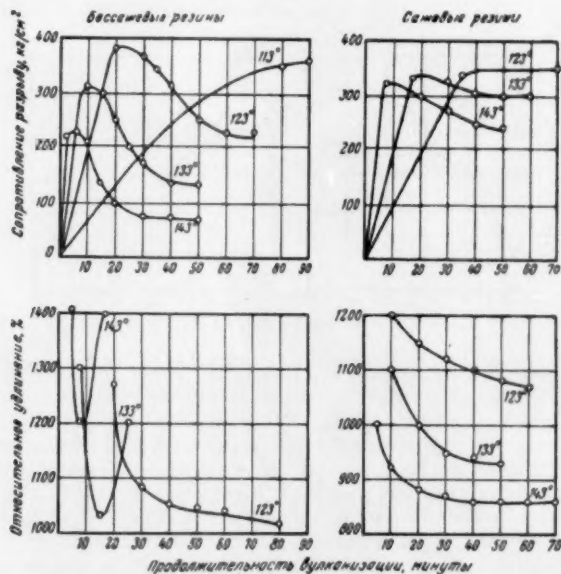
Fig. 6.—The kinetics of changes of tensile strength and ultimate elongation in SKI rubbers, with and without carbon black during vulcanization at different temperatures. Abscissa is vulcanization time in minutes. Left figures are for rubbers without carbon black and right are for rubbers with carbon black

These rubbers are characterized by optimum vulcanization with respect to tensile strength, which coincides with the beginning of reversion in ultimate elongation.

This indicates the simultaneous formation and breakdown of structure during the vulcanization of SKI, which is similar in rate to anologous processes in the vulcanization of NR[4].

Reversion of ultimate elongation during vulcanization occurs very rarely in butadiene-styrene rubbers and never in SKB rubbers.

With a rise in the vulcanization temperature the proportion of destructive phenomena increases. This is indicated by a decrease in the vulcanization plateau with respect to tensile strength and an increase in the degree of reversion in ultimate elongation (Figure 6).

The unfavorable effect of temperature, however (see Figure 6), may be attenuated by adding carbon black and using the properly selected type of vulcanization recipe.

The correct selection of a vulcanization recipe (the type of accelerators, their combination, and the proportion of accelerators to sulfur) is very important in the case of SKI and other rubbers with a tendency towards degradation.

Naturally, such a selection should not be made without taking into account the specific effect of the various carbon blacks and softeners on the processes occurring during vulcanization, including the reactions of sulfur, oxygen and the accelerators with rubber and with each other.
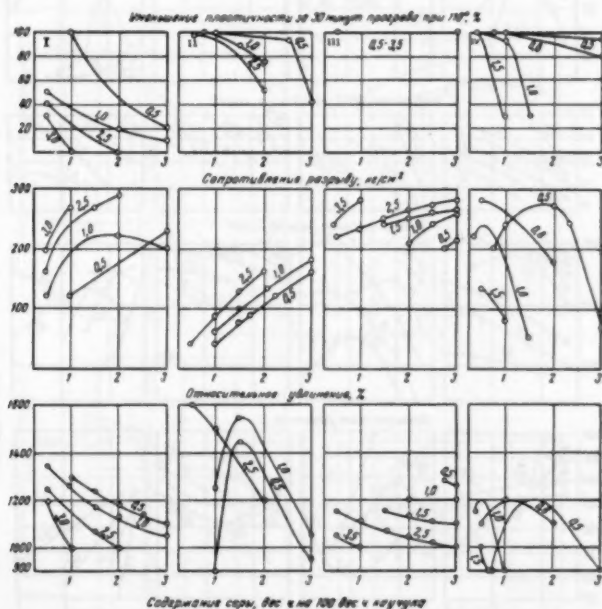
FIG. 7.—The dependence of the properties of unfilled SKI rubbers on the vulcanization parameters (the content of sulfur is indicated on the abscissas, the content of accelerator on the curves). Decrease in plasticity after 30 min heating at 110° C, %, top row of figures; tensile strength, kg/cm², middle row of figures; ultimate elongation, %, bottom row of figures. Vertical rows of figures are: I—diphenylguanidine; II—MBT; III—MBTS; IV—thiuram.

Thus the same problems arise in selecting vulcanization recipes for SKI rubbers as for other rubbers.

Figures 7 and 8 show that great variation in the properties of SKI vulcanizates may be obtained through the slection of vulcanization recipes. They also show the resistance of SKI rubbers to premature vulcanization (the maintenance of plasticity in comparison with initial plasticity after exposure to heat for 30 minutes at 110° C), tensile strength at optimum vulcanization, ultimate elongation at break, and moduli at 300 per cent elongation.

SKI and other highly elastic polymers (such as NR, butyl and polychloroprene rubbers) which show a crystalline structure upon elongation even when active fillers are not used, are characterized by high tensile strength.

When the testing temperature is increased, the tensile strength of unfilled SKI vulcanizates decreases more than that of NR vulcanizate but less than that of chloroprene or butyl rubber vulcanizates (Figure 9).

It is also shown that when the temperature is increased ultimate elongation in SKI vulcanizates decreases less than in vulcanizates of other synthetic rubbers. This indicates a greater homogeneity in the molecular structure of SKI

Fig. 8.—The dependence of the properties of SKI rubbers containing 30 parts of channel black by weight on the vulcanization parameters (content of sulfur, phr, is indicated on the abscissas, and content of accelerator is indicated on the curves). Decrease in plasticity after 30 min heating at 110° C, %, top row of figures; modulus at 300% elongation, kg/cm², second row of figures; tensile strength, kg/cm², third row of figures; ultimate elongation, %, fourth row of figures. Vertical rows of figures are: I—diphenylguanidine; II—MBT; III—MBTS; IV—thiuram.

vulcanizates, resulting in a more even distribution of tension in stretched samples[5], and consequently more favorable conditions for the orientation of molecular chains during deformation.

With a rise in the testing temperature changes in the tensile strength and ultimate elongation of unfilled SKI rubbers depend to a great extent on the homogeneity of the molecular structure, which in turn is determined by the particular polymerization process used (Figure 10).

The tensile strength of SKI rubbers at normal and especially at high temperatures is increased by adding channel black.

Optimum loading for SKI rubbers with respect to tensile strength is 30 parts of channel black per 100 parts of rubber at normal temperatures, and 50 parts of channel black at 100° C.

Table I shows the properties of unfilled SKI and other synthetic rubbers; Table II that of the same rubbers with an optimum loading of channel black.

These tables provide data on the abrasion resistance of SKI rubbers as measured by a Grasselli abrader, and show that in resistance to abrasion SKI is somewhat inferior to NR.
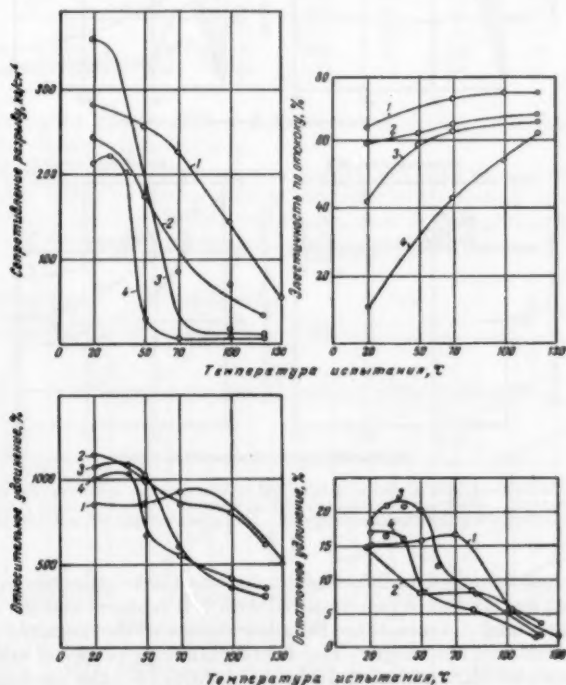
Fig. 9.—The dependence of tensile strength (upper right), ultimate elongation (upper left), permanent set (lower left), and rebound elasticity (lower right) of unfilled NR (1), SKI (2), "nairite" (3) and butyl rubber (4) on temperature, ° C.

A more detailed study of abrasion resistance in SKI rubbers was made with a new device on which rubber samples are oscillated against different abrasive surfaces with varying radial and braking loads. Information on the apparatus and methods for testing abrasion in vulcanizates will be given in one of the following issues of this periodical.

Data in Figure 12 shows that with a low coefficient of friction and a corresponding percent slip, SKI rubbers differ little from NR rubbers.

The resistance of SKI rubbers to thermal oxidative aging depends on the composition of the rubber, i.e., the type of vulcanization recipe, age resistors, softeners, etc. used.
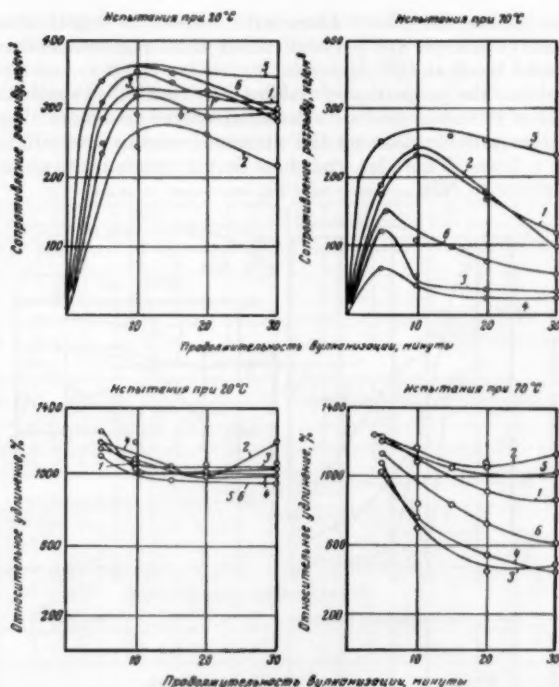
Fɪɢ. 10.—The thermostability of various unfilled SKI rubbers (numbers on curves refer to SKI rubbers of different structure). Abscissa is vulcanization time in minutes. Ordinate (upper) is tensile strength in Kg/cm² and (lower) ultimate elongation in per cent. Left is for testing at 20° and right is for testing at 70° C.

This report is limited to information showing the relationship in SKI rubbers between age resistance (as compared with NR rubbers) and the amount of channel black used (Figure 13). Detailed studies of the dynamic properties of SKI rubbers were also made. The chief dynamic properties of rubber are its dynamic modulus (E) and internal friction modulus (K), the mechanical losses

TABLE I

PROPERTIES OF UNFILLED SKI, NR AND OTHER SYNTHETIC RUBBERS

Rubbers	Tensile strength, kg/cm²		Ultimate elongation, %		Rebound elasticity, %		Brittle temp., ° C
	At 20° C	At 100° C	At 20° C	At 100° C	At 20° C	At 100° C	
SKI	300	80	1000	700	65	75	−56
NR	360	150	850	1100	75	80	−58
SKB	20	8	700	350	45	54	−50
SKS-30A	25	13	800	400	56	67	−52
Chloroprene	340	30	950	400	53	66	−43
Butyl rubber	220	15	900	350	12	55	−55
Polyisocyanate	316	325	550	300	35	63	−45

TABLE II

PROPERTIES OF SKI, NR, AND OTHER SYNTHETIC RUBBERS WITH AN OPTIMUM LOADING OF CHANNEL BLACK

Rubbers	Tensile strength, kg/cm²		Ultimate elongation, %		Rebound elasticity, %		Resistance to tear, kg/cm	Resistance to abrasion, cm²/kw-hr
	At 20° C	At 100° C	At 20° C	At 100° C	At 20° C	At 100° C		
SKI	320	145	990	880	49	59	65	400
NR	360	200	650	750	60	72	100	300
SKB	170	60	600	220	26	41	60	450
SKS-30A	260	120	730	450	35	46	80	260
Chloroprene	265	70	760	360	47	68	70	290
Butyl rubber	240	110	820	980	9	35	65	250

suffered during a loading cycle per unit volume of the sample tested times the square of its dynamic deformation.

Both these dynamic characteristics depend not only on the temperature, but to a great extent on the mechanical character of the testing, which in itself is determined by the type of deformation experienced (elongation, shear, compression, etc.), its amplitude, frequency, etc. It was therefore deemed neces-
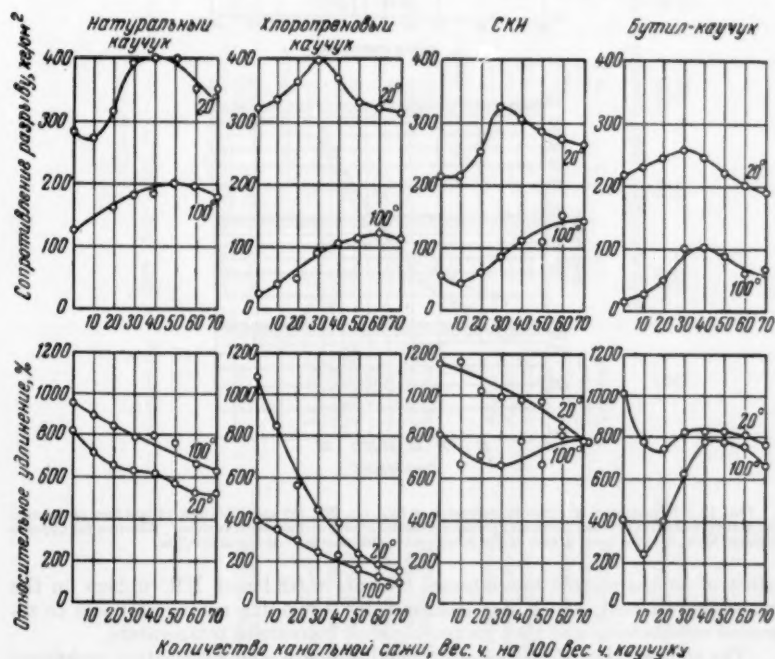
FIG. 11.—The dependence of tensile strength and ultimate elongation on the amount of channel black used in SKI, NR, polychloroprene and butyl rubbers (tested at 20° C and 100° C). Ordinate for upper row of figures is tensile strength in kg/cm² and for the lower row is ultimate elongation in per cent. Reading from left to right the figures are for natural rubber (first row), chloroprene rubber (second row), SKI (third row), and butyl rubber (fourth row). The abscissa is phr of channel black.

sary to present the results of several experiments, where different testing methods were used (Table III).

Table III indicates that the dynamic properties of SKI rubbers are very similar to those of NR rubbers. The low internal friction modulus in SKI rubbers is particularly important, as it enables these rubbers to perform satisfactorily under conditions of repeated deformation. Table III shows the favorable
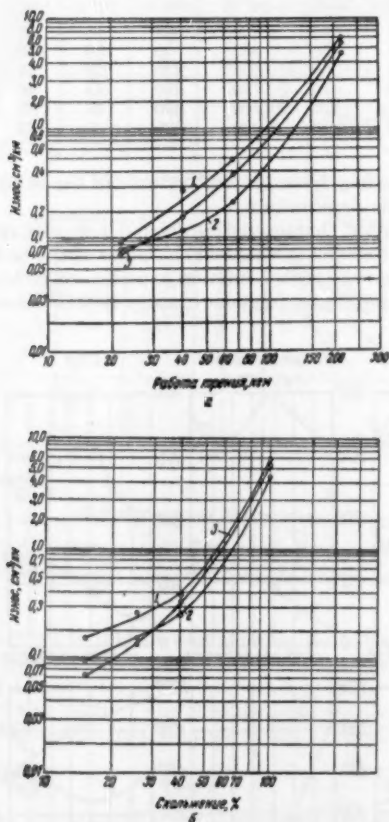
Fig. 12.—Dependence of abrasion resistance of SKI (*1*), NR (*2*) and SKS-30A (*3*) rubbers on friction (a) and rate of slip (b) when vibrated against a constantly renewed abrasion surface. Abscissa for upper is friction, kg-m, and for lower is rate of slip in percent. Ordinate is abrasion in cm³/km.

effect of comparatively low internal friction in SKI and NR rubbers on the generation of heat, which was measured by subjecting rubber stoppers to repeated compression and then measuring their increase in temperature.

The combination of high elasticity and strength, and satisfactory resistance to heat and oxidation, results in a high degree of fatigue endurance* in these rubbers.

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* Analyst's note: See Table IV for explanation of "fatigue endurance".

TABLE III

DYNAMIC PROPERTIES OF SKI, NR, SKS-30A AND CHLOROPRENE RUBBERS

Testing equipment and methods	Unit of measure	Unfilled rubber				Rubber containing 50 parts of channel black per 100 parts of rubber by weight				Literature references to methods
		SKI	NR	SKS-30A	Chloroprene	SKA	NR	SKS-30A	Chloroprene	
Dynamic modulus										
Kornfel'd device	kg/cm²	32	33	62	50	138	180	343	430	6
Biderman pendulum	kg/cm²	8	9	15	15	32	31	72	118	7
Rocking device	arbitrary unit	16	20	23	29	45	50	70	137	8
Free contraction	kg/cm²	11	15	20	20	47	54	60	80	9
Free vibrations	kg/cm²	12	15	28	23	29	25	37	—	10
Variable flexing	kg/cm²	13	10	15	—	—	—	—	—	11
Internal friction modulus										
Kornfel'd device	kg/cm²	1.9	1.7	7.4	4.0	28	39	90	112	6
Biderman pendulum	kg/cm²	1.5	1.2	6.0	3.2	14	12	39	59	7
Rocking device	arbitrary unit	1.5	1.6	4.2	2.8	8	9	12	13	8
Free contraction	kg/cm²	1.8	2.1	7.2	4.5	19	21	28	—	9
Free vibrations	kg/cm²	1.5	1.7	3.8	2.9	16	12	—	—	10
Variable flexing	kg/cm²	3.6	3.3	5.2	—	—	—	—	—	11
Heat generation under repeated compression										
At a given deformation	°C	50	59	108	89	121	122	135	158	
With a given load	°C	67	73	92	85	123	129	144	160	
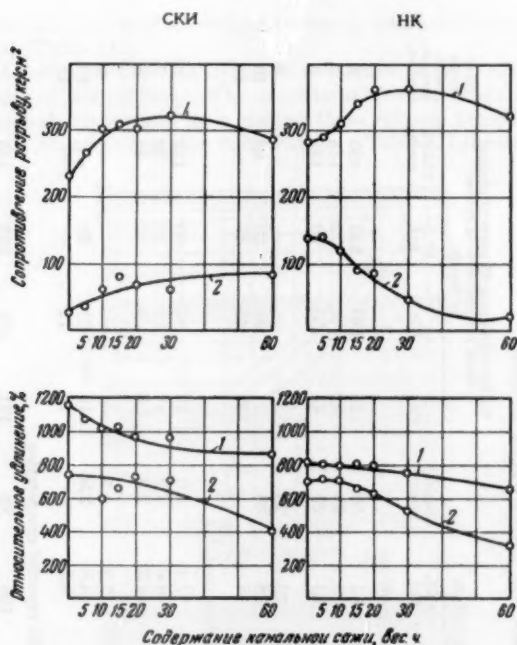
Fig. 13.—Thermal oxidation resistance of SKI and NR rubber containing various quantities of channel black. Abscissa is amount of channel black, in parts by weight. *1*—under normal conditions; *2*—after aging for 72 min at 100° C. Upper left is tensile strength, kg/cm², of SKI and lower left is ultimate elongation of SKI. Upper right is tensile strength of NR and lower right is ultimate elongation of NR.

Samples of SKI and NR rubbers, some containing 30 parts of carbon black by weight and others containing no channel black at all, were tested on a machine built by the "Metallist" Plant; the results of these tests are shown in Table IV. Results obtained with unfilled SKI, NR and other rubbers tested on the "Metallist" Plant machine and on a dynamic relaxometer[12], which effects repeated elongation under a constant load, are shown in Table V. Table VI

TABLE IV

FATIGUE ENDURANCE OF SKI AND NR RUBBERS, EXPRESSED IN UNITS OF TIME (MINUTES) REQUIRED TO DESTROY SAMPLES WHEN SUBJECTED TO REPEATED ELONGATION ON A MACHINE BUILT BY THE "METALLIST" PLANT

	Testing conditions					Rubbers containing 30 parts of channel black to 100 parts of rubber (by weight)	
Elonga-tion (from-to), %	Num-ber of defor-mation/ cycles min.	Test-ing temp., °C	Whether perfo-rated or not before testing	Unfilled rubbers			
				SKI	NR	SKI	NR
0-100	250	20	no	4113	521	2448	175
0-100	250	100	no	—	—	526	290
0-200	250	20	no	250	77	101	53
0-200	250	20	yes	113	31	37	25
0-200	500	20	no	95	30	85	26
100-250	250	20	no	>6960	>6960	>7200	10,140
100-200	250	20	yes	>1380	>10,490	>7900	8730

TABLE V

FATIGUE ENDURANCE OF SKI, NR AND OTHER SYNTHETIC RUBBERS EXPRESSED IN UNITS OF TIME (MINUTES), REQUIRED TO DESTROY SAMPLES WHEN SUBJECTED TO REPEATED ELONGATION WITH A CONSTANT TERMINAL LOAD (1), AND A CONSTANT TERMINAL STRAIN (2)

Testing condition			Rubber					
Type of elongation	Elongation (from-to), %	Testing temperature, °C	SKI	NR	SKS-30A	SKB	Chloroprene	Butyl rubber
(1)	0–200	20	220	110	—	19	64	82
(2)	0–200	20	210	74	8	84	73	180
(2)	0–200	60	170	82	2	—	—	11
(2)	0–200	100	210	85	1	14	—	6
(2)	0–50	20	—	2100	—	1500	—	—
(2)	0–100	20	5400	380	—	1040	1500	150
(2)	0–200	20	210	74	—	84	73	180
(2)	0–300	20	70	40	—	4	14	—

Note: Data on fatigue efficiency of SKS-30A, SBK, chloroprene and butyl rubbers obtained from V. G. Epshteyn and B. K. Karmin.

compares the fatigue endurance of breaker-type rubbers from NR and SKI containing "burner" black, under varying magnitudes of flexing.

The tests were made at an operating cycle of 0.1 j/cm² and at temperatures close to those existing in the breaker zone of an operating 260–20 tire made from NR and SKI, and run on an "IPZ-1" machine (a drum with 20 mm cleats) at the rate of 50 km/hr with a 1550 kg load.

Data in Tables IV, V, and VI indicate that when subjected to the most diverse types of repeated deformations the fatigue endurance of SKI rubbers is similar to that of NR rubbers.

TABLE VI

FATIGUE ENDURANCE OF SKI AND NR BREAKER RUBBERS, CONTAINING "BURNER" BLACK, UNDER BACK-AND-FORTH VARIABLE FLEXING

Rubber	Dynamic properties of rubbers, kg/cm²		Surface temp. of samples, °C	Amplitude of deformation, %	Fatigue efficiency in millions of cycles
	E	K			
SKI	24.6	4.4	83	28	9.0
NR	31.2	4.1	74	25	10.7

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SKI RUBBER, A NEW POLYISOPRENE *

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All-Union Research Institute of Synthetic Rubber

It is known that the industrial synthesis of general purpose rubbers has been accomplished and has been developing on the basis of the use of divinyl as the starting monomer, taken either in the pure state (sodium-divinyl rubber) or in mixture with another monomer—styrene (divinylstyrene rubber). However, synthetic polymers of isoprene have, to this day, found no practical application despite the fact that natural rubber (NR) is a polyisoprene and the first samples of synthetic rubber were obtained from isoprene. This is explained by the circumstance that, up to the present time, it was not possible to synthesize an isoprene or a copolymer-isoprene rubber which would have substantially improved properties over a similar rubber obtained on the base of divinyl; in addition isoprene is a less plentiful raw material than divinyl.

Divinyl rubbers differ from natural rubber not only in their microstructure but also in the chemical nature of the link of the polymer chain; and still, with time, they successfully replaced natural rubber in the production of a large number of rubber goods. At the same time, due to various new properties possessed by the divinyl rubbers, their application led to the improvement in the quality of certain goods and, in many cases, to a simplification and reduction in cost of production of the latter.

Nevertheless even the most modern general purpose commercial rubbers, which are obtained from divinyl, possess various substantial shortcomings in comparison with natural rubber. The most significant shortcoming of the divinyl rubbers is their reduced elasticity. This shortcoming is especially significant all the more, since rubber mixes with these rubbers as a base must, because of their low strength, be prepared with a large content of carbon black. For this reason such rubbers cannot serve as an equivalent substitute for natural rubber in carcass and breaker rubbers for tires, especially truck tires, and in the manufacture of various technical and also household, highly elastic goods.

At the All-Union Research Institute of Synthetic Rubber (VNIISK), the staff has, under the direction of A. A. Korotkov, accomplished the synthesis of isoprene rubber of a new type[1], which has been given the abbreviated designation SKI. Starting in 1955, various brief communications have appeared in foreign journals, from which it follows that methods have been developed in the US for the preparation of isoprene rubber with a structure and properties close to natural rubber (see, for example, F. W. Stavely, *Rubber World* 133, No. 1, 83 (1955); *Rubber Age* 76, No. 4, 588 (1955); 78, No. 1, 99 (1955)). According to A. A. Korotkov, K. B. Piotrovskiĭ, and D. P. Feringer, the polymer chains of SKI contain 90–95% links joined in the position 1,4 and only 5–10% links joined in the position 1,2 and 3,4. According to K. V. Nelson and I. Ya. Poddubniĭ, the predominant portion of the 1,4 links in the SKI is in the *cis* form, while the

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side groups consist primarily of 3,4 links (6–7%). Because of the absence of acetonylacetone in the decomposition products of the ozonides of SKI, A. I. Yakubchik, S. K. Zykona, and V. M. Vlasova established that the 1,4 links in the molecular chain of SKI, just as in natural rubber, are joined to each other only in the position 1,4–1,4 ("head to the tail"). It is known that the molecular chains of natural rubber are almost entirely built of *cis*-1,4 links which are joined to each other in the position 1,4–1,4. Thus SKI is very close to natural

TABLE I

COMPARATIVE PROPERTIES OF SKI AND NATURAL RUBBER

1	2 Temperature of test, °C	3 SKI		4 Natural rubber	
		Unfilled mix	Black mix	Unfilled mix	Black mix*
Strength characteristics:					
Modulus, kg/cm²:					
at 300% elongation	20	8–12	25–30	15	33
at 500% elongation	20	11–24	35–50	35	107
Resistance to rupture, kg/cm²	20	230–320	300–380	260–330	325–400
Relative elongation, %	20	1100–1300	950–1050	800–850	750–850
Residual elongation, %	20	10–16	38–44	10–12	30–38
Resistance to rupture, kg/cm²	70	120–180	180–220	240	220
Relative elongation, %	70	1000–1200	1000–1100	900	900
Resistance to rupture, kg/cm²	100	—	110–150	—	180
Relative elongation, %	100	—	900–1000	—	950
Resistance to tear, kg/cm²	20	—	75–85	—	130–150
Dynamic elastic properties:					
Elasticity against rebound on KS pendulum**, %	20	85	69	82	58
	100	89	74	88	61
Elasticity against rebound (Schaub), %	20	62–70	50–55	69	50
	100	67–79	58–64	74–76	—
Dynamic modulus of elasticity**, kg/cm²	20	23	52	21	83
	100	21	43	21	48
Modulus of friction, 10⁴dn/cm²	20	188	1000	216	2300
	100	127	675	142	1200
Temperature during repeated compression, °C:					
Constant deformation (40%)	20	52	80	50	80
Constant load (177 kg)	20	74	88	75	92
Temperature during sign-changing bending***, °C	20	25.8, 50	26.9, 108	25.5, 66	25.3, 126****
Strength characteristics after aging at 100° for 48 hrs:					
Resistance to rupture, kg/cm²	20	210–250	—	220–270	—
Relative elongation, %	20	850–900	—	650–750	—
Strength characteristics after aging at 100° for 72 hrs:					
Resistance to rupture, kg/cm²	20	—	240–290	—	100–150
Relative elongation, %	20	—	800–850	—	500–600
Coefficient of frost resistance during 100% stretch	−45	0.8–0.9	0.5–0.6	0.8–1.0	—

* Mix contains 30 weight parts of channel black per 100 weight parts of rubber.
** According to Ye. V. Kuvshinskiǐ and Ye. A. Sidorovich (VNIISK).
*** The second figure is the elongation in %.
**** Run of this specimen—180 min; others—360 min.

rubber in its molecular structure. It was shown by I. Ya. Poddubniǐ, Ya. G. Erenbury, and V. G. Nazarov that SKI is close to natural rubber also in its molecular-weight distribution.

L. A. Chernikina and B. K. Karmin (All-Union Research Institute of Tire Industry) have established, on the basis of x-ray analysis that SKI has the capacity to crystallize during stretching. Later, the capacity of SKI to crystallize was established also by M. P. Votinov (Leningrad Polytechnic Institute, M. I. Kalinin) on the basis of the Joule effect which was observed during the stretching of vulcanizates of SKI. However, in view of the somewhat lesser regularity of the structure, SKI crystallizes with a noticeable speed only during greater elongation than that required for natural rubber.

The closeness of the structures of SKI and natural rubber determines the large similarity of their mechanical properties; however, since these rubbers are not identical, certain differences are observed in their properties; according to some characteristics, SKI is inferior to natural rubber, while according to others, it is equivalent to or excels it (Table I).

It is seen from Table I that SKI, as with natural rubber and other crystallizing rubbers, has a high resistance to rupture in an unfilled mix; besides, as regards the strength limit calculated on the basis of the original cross-section of the test specimen; for both unfilled and carbon black vulcanizates, the best specimens of SKI are on a level with natural rubber. At the same time, vulcanizates of SKI have a considerably much higher relative elongation than vulcanizates of natural rubber. For this reason, the true strength of SKI is much greater than that of natural rubber.

In passing, it is necessary to point out that the strength characteristics of rubbers made of SKI as well as of natural rubber depend to a great extent on the composition of the sulfur-accelerator system therein and on the conditions

Figure 1
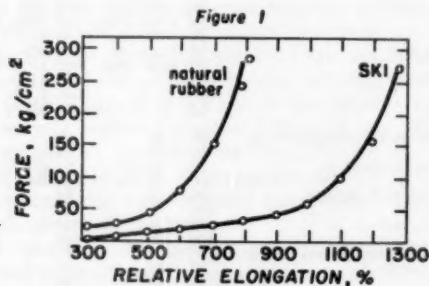
of their vulcanization. Resistance to rupture of SKI in a simple mix of rubber + sulfur is about 200 kg/cm². The use of organic accelerators makes it possible to increase the resistance to rupture of unfilled mixes of SKI up to 300 kg/cm² and higher and that of carbon black mixes (mixes with channel black) on the average up to 350 kg/cm².

Along with a much higher relative elongation, vulcanizates of SKI have a considerably much lower modulus than vulcanizates of natural rubber. This is distinctly seen also from Figure 1 which shows typical force—elongation curves for unfilled rubber of SKI and of NR. Much lower values of the modulus, as well as a greater relative elongation, characterize a much greater elasticity of the rubber under static conditions. For this reason, the valuation of SKI and NR on the basis of these properties tends to favor the synthetic rubber.

At the same time, vulcanizates of SKI have high dynamic elastic properties. On the basis of indications of elasticity against rebound, dynamic modulus of elasticity, and modulus of friction, both at room and higher temperatures, SKI in an unfilled mix is practically equivalent to NR, while in a carbon black mix, it has a distinct advantage over it (the modulus of friction characterizes the absolute losses in rubbers which operate under conditions of constant deformation). From the results of tests of repeated compression (under constant load

and constant deformation) and repeated sign-changing bending, it can be seen that unfilled vulcanizates of SKI are characterized by practically the same heat formation, while carbon black vulcanizates are characterized by a noticeably smaller heat formation than similar vulcanizates of natural rubber. Thus, the cited data show that, on the basis of the total complex of elastic properties, SKI exceeds to a certain extent even natural rubber.

By comparing the examined properties of SKI and NR in connection with their structures, one must come to the conclusion that the known disturbance of the regularity in the build up of the polymer isoprene chain can impart to the synthetic polymer much higher strength and elastic properties than the corresponding properties of natural rubber.

However, on the basis of certain other mechanical properties SKI is inferior to NR. Thus, SKI, both in an unfilled as well as in a carbon black mix, has a much lower resistance to tear. A further substantial shortcoming of SKI is its much lower temperature resistance (retention of strength characteristics at increased temperatures). But here, it is necessary to point out that, in the presence of carbon black, the temperature resistance of SKI improves, while the temperature resistance of natural rubber, on the other hand, decreases. For this reason, in a carbon black mix, the temperature resistance of SKI is below that of natural rubber to a smaller extent than in an unfilled mix.

It is also necessary to point out that resistance to tear and temperature resistance of SKI depend on the conditions of its preparation and, at the present time, ways of improving the indicated properties of this rubber are being projected. It is obvious that the lower resistance to tear and temperature of SKI are explained by its smaller, in comparison with NR, capacity to crystallize. Consequently, in this case, the insufficient regularity in the structure of the SKI plays a negative role.

Due to the increased content of 1,2–3,4 links in the polymer chain of SKI, it has a somewhat higher temperature of vitrification (on the average $-68°$ against $-70°$ for natural rubber) and a somewhat lower coefficient of frost resistance, especially at a much lower temperature. Nevertheless, in view of the lesser crystallizability, SKI is more suitable than natural rubber for the manufacture of certain frost-resistant goods.

On the basis of heat resistance (resistance to thermal aging), SKI in unfilled mixes is practically equivalent to NR while in carbon black mixes, it exceeds NR considerably.

SKI differs from natural rubber in its technological (working) properties. Thus, unvulcanized mixes of SKI have a lower strength and adhesiveness than mixes of NR; unfilled mixes of SKI are not calendered and sprayed satisfactorily. Thus, on the basis of these properties, SKI is similar to ordinary synthetic rubbers obtained from divinyl. However, as distinct from the latter, SKI has a noticeably expressed capacity for rolling during mechanical working. In addition, SKI has a considerably smaller shrinkage than divinyl rubbers. At the same time, during working under ordinary conditions, SKI is spread worse in mixes with channel black than are divinyl rubbers. In order to obtain such mixes of SKI with good working properties, it is necessary to roll it and use special softeners.

Despite the existence of the various indicated shortcomings of SKI, it can be assumed that, as a result of broad investigations presently being carried on in order to improve the quality of the polymer as well as to perfect the technique

of its processing, the use of SKI will, in the final analysis, make possible successfully replacing NR in all goods in which the latter still retains advantages over synthetic rubbers.

In conclusion, it is necessary to point out that the fact of the synthesis of this new type of isoprene rubber is not only of great practical interest but is also of exceptionally important significance for the further development of the entire field of rubber synthesis, because the ways of creating rubbers equivalent to natural rubber as regards the complex of elastic properties have remained unknown up to now.

REFERENCE

Compare the preceding article, this issue.

THE MUTUAL SOLUBILITY OF POLYMERS. I. PHYSICOMECHANICAL PROPERTIES OF STOCKS PREPARED FROM A MIXTURE OF POLYMERS *

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In recent years the use of mixtures of different polymers for the production of parts having a desired combination of properties not found in pure polymers has grown steadily. Thus the necessity has arisen for a detailed study of the properties of polymer mixtures and for the formulation of theoretical principles which would enable one to make a deliberate choice of mixed polymers for the solution of practical problems. The aim of our work was to study the basic principles underlying the mixing of polymers, using a mixture of rubbers as an example. Besides this, the study of the relation between the mechanical properties of rubber stocks and the type and proportions of the mixed rubbers is of great practical and theoretical interest.

It is known that rubbers are liquids, and that a solution of them in a low molecular weight solvent can be considered, thermodynamically speaking, as a mixture of two liquid phases[1]. It is quite clear that the mixing of two amorphous polymers, and in particular of two rubbers, should likewise be considered as the mutual solution of two liquid phases. An essential feature of such systems is the very high viscosity of both components of the solution (the polymer mixture), which brings about some very unusual effects resulting from the chain structure of the large polymer molecules. The study which we made earlier[2] of the properties of mixtures of two polymers, and also of cured stocks prepared from such mixtures, showed the accuracy of this approach to the process of polymer mixing, and made it possible to clarify the basic principles of mutual solubility of amorphous polymers. Measurements of the heats of mixing of polymers with one another, which were made[3] for many pairs of polymers, confirmed this conclusion and made it possible to understand the nature of the mutual solubility of polymers in relation to the chain structure of their molecules. In line with the ever-increasing interest in the problems of mixing polymers, which is revealed in the increasing number of papers devoted to this question[4], we have found it necessary to publish a more detailed presentation of our results, since our earlier work[5] is not widely available.

Samples for testing and their preparation.—The rubbers chosen for this research, differing in their chemical composition and structure, were as follows: natural rubber, polybutadiene rubber (SKB), butadiene-styrene rubbers (SKS-30 and SKS-10) and butadiene-nitrile rubber (SKN). Each rubber was studied both individually and in combination with each of the other rubbers. The recipes chosen for the rubber stocks were typical, with a content of 50 parts by weight of channel black on 100 parts of rubber (or the mixture of rubbers) and all with the same type of curative system, containing sulfur and Captax.

The stocks were mixed on a rubber mill in two stages.   First all the ingredients were added to each rubber separately.   Then the masterbatches thus obtained were weighed out in the necessary proportions and were mixed together on a rubber mill for 15 minutes.   Such a method of preparing the mixed stocks insured the most complete and uniform distribution of the ingredients in the rubbers and a mutual mixing of the latter.
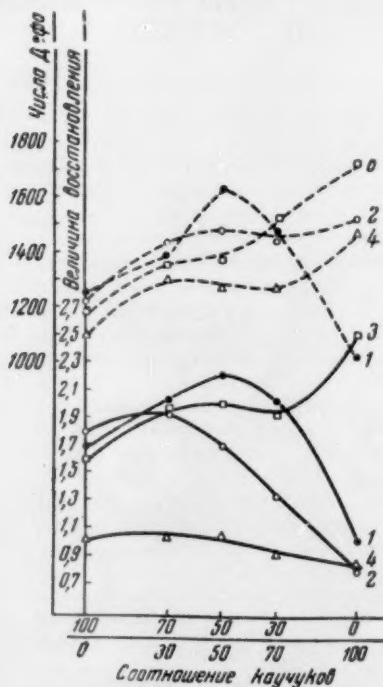
Fig. 1.—Plastic-elastic properties of combined uncured rubber stocks.   1—SKS-30 + SKB; 2— SKS-30 + natural rubber; 3—SKS-30 + SKS-10; 4—SKB + natural rubber. Solid lines—recovery value; broken lines—Defo number.   The abscissa represents the proportions of the rubbers in per cent; the outer ordinate represents the Defo number, the inner one the recovery figure.

The mixed rubbers, i.e., the uncured rubber stocks prepared from a base of the combination of rubbers, and the cured stocks obtained from these were all tested.   The present work gives the results obtained by testing such stocks through the usual standard methods for the physico-mechanical evaluation of cured and uncured rubber stocks[6].

Results.—The most important control operation carried out in the process of preparing raw rubber stocks is the measurement of plasticity and recovery values.   The corresponding characteristics (Defo numbers and recovery values) are given in Figure 1 in relation to the proportions of the rubbers in the stock.   As the figure shows, mixtures of SKS-30 and SKB rubbers in certain proportions have higher Defo and recovery values than rubber stocks containing only a single rubber (the outside points on the curves correspond to rubber

stocks prepared from one type of rubber and with the same added ingredients). This indicates that the mixing of SKS-30 and SKB rubbers causes a rise in the elastic properties and a decrease in the plasticity. It is interesting to note that while the properties of all the other mixtures change in relation to the propor-
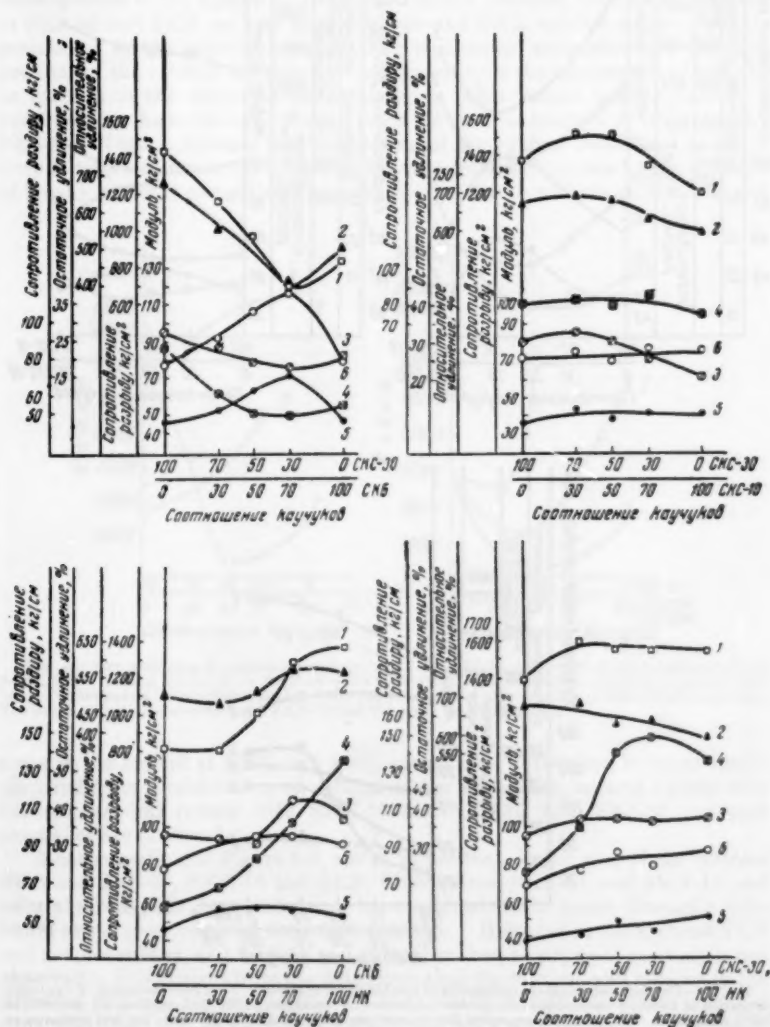
FIG. 2.—Physicomechanical characteristics of the combined cured stocks. 1—Tensile strength; 2—relative (per cent) elongation at break; 3—permanent set; 4—tear resistance; 5—modulus at 200% elongation; 6—modulus at 300% elongation. The abscissas represent the proportions of the rubbers in per cent; the first ordinates at left represent the tear resistance in kg/cm, the second the permanent set in per cent, the third the per cent elongation at break, the fourth the tensile strength in kg/cm², and the fifth the modulus of elasticity in kg/cm². "HK" = "natural rubber", "CKC" = "SKS", CKB = "SKB".
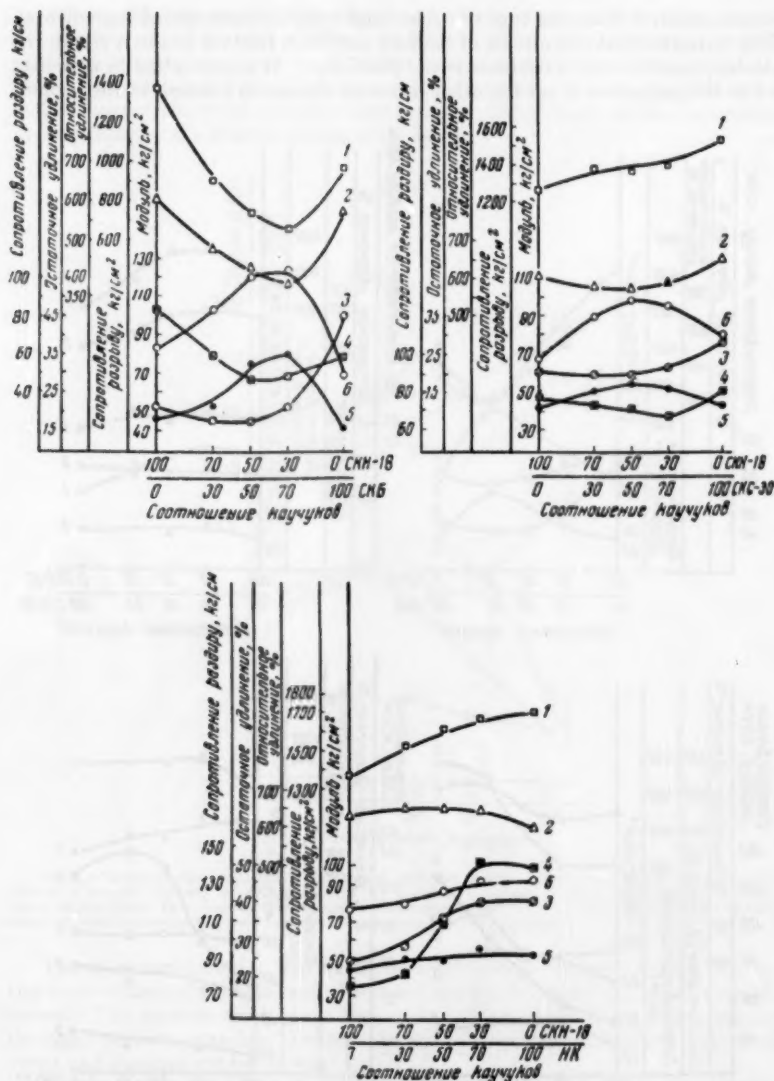
Fig. 3.—Physicomechanical characteristics of combined cured stocks. 1—Tensile strength; 2—per cent elongation at break; 3—permanent set; 4—tear resistance; 5—modulus at 200% elongation; 6—modulus at 300% elongation.   The abscissas represent the proportions of the rubbers in per cent; the first ordinates at left represent the tear resistance in kg/cm, the second the permanent set, the third the per cent elongation at break, the fourth the tensile strength in kg/cm², and the fifth the modulus in kg/cm³.   "CKH" = "SKN".   Also see note under Figure 2.

tion of rubbers more or less gradually, no maximum or minimum being noted, the mixture of SKS-30 and natural rubber does show a maximum on the curve of the relation between recovery value and proportion of rubber.

The standard criteria used for evaluation of the quality of vulcanizates are tensile strength, per cent elongation at break, permanent set, tear resistance, modulus of elasticity and dynamic flex life (flex resistance). The corresponding data for a series of systems are given in Figures 2–4. It is evident from a consideration of the figures that the cured stocks prepared from a combination of SKS-30 and SKB, as well as of SKN-18 and SKB, exhibit a characteristic peculiarity in the relation between their mechanical properties and the proportions of the rubbers in them. This peculiarity is the appearance of minima or maxima in the curves of these relations. This feature also appears in a much weaker form in cured stocks prepared from a mixture of SKN-18 and SKS-30. Thus it appears that the mixing of the rubbers mentioned causes a drop in tensile strength (as related to the true cross-section area at the moment of break), per cent elongation at break, tear resistance and permanent set, and
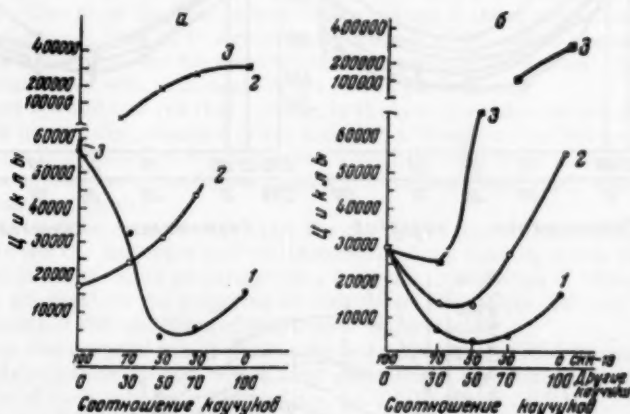
Fig. 4.—Flex resistance of combined cured stocks. a: 1—SKS-30 + SKB; 2—SKB + natural rubber; 3—SKS-30 + natural rubber; b: 1—SKN-18 + SKB; 2—SKN-18 + SKS-30; 3—SKN-18 + natural rubber. The ordinate is the number of flexing cycles and the abscissa the proportions of the rubbers in per cent. The upper scale of the abscissa is for SKN-18 and the lower for "other rubber".

a rise in the moduli at 200% and 300% elongation. However, in cured stocks prepared from combinations of natural rubber with SKB, natural rubber with SKS-30, natural rubber with SKN-18 and SKS-10 with SKS-30, no such anomalies are observed.

A consideration of Figure 4 a, and b, shows that, in the case of the systems SKB and SKS-30, SKN-18 and SKB, SKN-18 and SKS-30, and SKN-18 and natural rubber, the flex-resistance of the combined stocks passes through a minimum as the proportions of the rubbers change. However, in the systems SKB and natural rubber, and SKS-30 and natural rubber, this type of anomaly is not observed. It is evident from the data given that the maxima and minima in the curve of property vs composition are most clearly revealed in stocks prepared from a combination of SKB with SKS-30 and SKB with SKN-18. The anomalous properties of the mixture of the nonpolar rubber SKB with the polar rubber SKN-18 should, of course, be attributed to the sharp difference in the character of the intermolecular reactions; but the appearance of this type of anomaly in mixtures of two nonpolar hydrocarbons—SKB and SKS-30—is unexpected and very interesting.
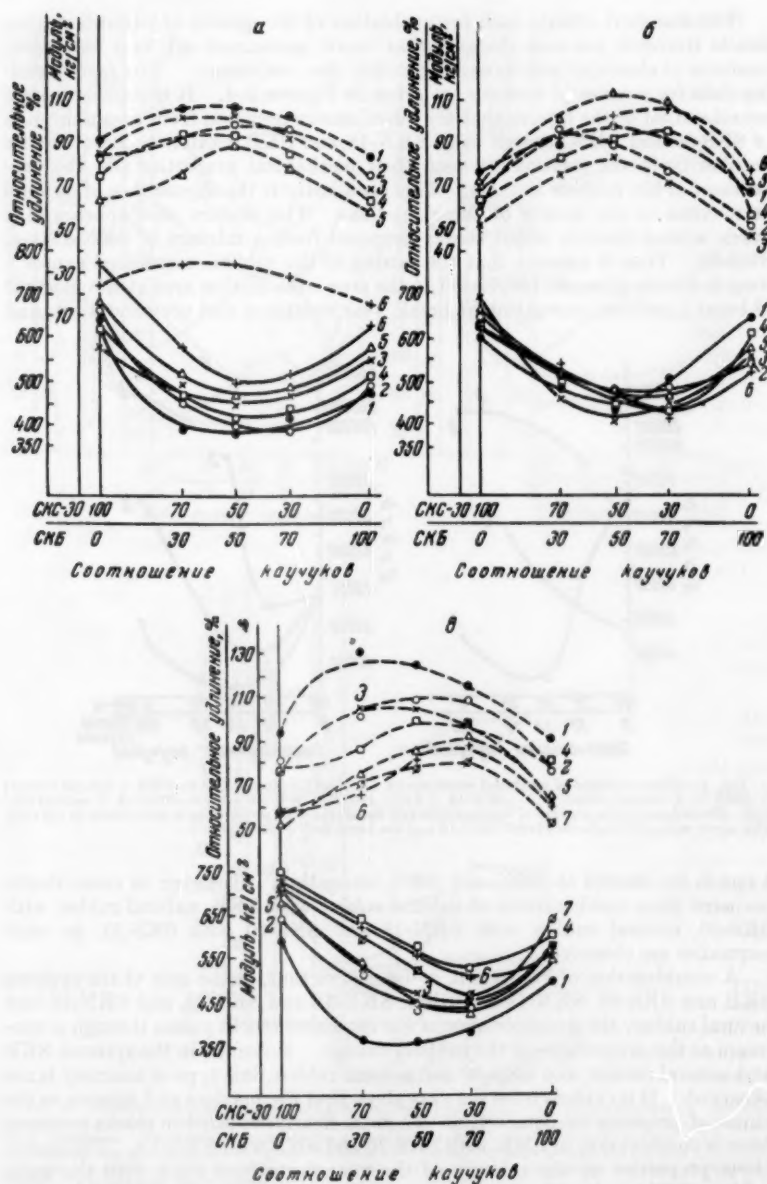
Fig. 5.—Effect of: *a* (upper left)—fillers, *b* (upper right)—accelerators, *c* (lower)—softeners on the mechanical properties of combined cured stocks (mixtures of SKS-30 with SKB). In *a*: *1*—oil black; *2*—lamp black; *3*—mixture of oil and channel black; *4*—furnace black; *5*—channel black; *6*—kaolin. In *b*: *1*—Altax and diphenylguanidine in SKS-30 + Captax in SKB; *2*—thiuram in SKS-30 + Captax in SKB;

It was necessary to find out upon which factors the above-mentioned anomalies in the properties of rubber stocks depend. For this purpose we have studied the effects of various technological and compounding factors. It might have been conjectured that the rubber was simply not well mixed, and that this caused the anomaly. Various fillers, accelerators and softeners were tried out for the purpose of improving the mixing of SKS-30 with SKB.

The use of fillers with varying reinforcement powers (channel black, oil black, lamp black, furnace black and combinations of these, as well as the mineral filler kaolin), as Figure 5a shows, do not change the basic anomaly observed in mixtures of SKS-30 with SKB. The maximum of the per cent elongation at break and the minimum of the modulus of elasticity at 300% elongation are visible in the curves of these properties vs the proportion of the rubbers, for all types of fillers used. The effect of the filler is revealed only in the change in the absolute values of the properties, and not in the nature of the relation. One must also bear in mind that a change in the channel black loading (in the range from 50 to zero parts by weight) also does not eliminate the anomaly in question, but has an effect on its magnitude; the anomaly becomes more pronounced with an increase in the carbon black loading.

Figure 5, b and c, shows that a change in the type of accelerator and softener does not cause a disappearance of the anomaly, although it does have an effect on the absolute values of the properties. We have also made a study of the influence of various technological factors (the mixing conditions), which also gave analogous results.

From all these data we may draw the conclusion that the anomalous relation between the properties and the proportion of the rubbers, which we have observed in cured stocks prepared from a base of a combination of SKS-30 and SKB, is governed by the properties of the rubbers themselves, and not by the ingredients nor the conditions of preparation of the stocks.

It was also essential to test stocks prepared from a base of SKS-30 combined with polybutadiene rubbers which were polymerized in different ways. For examples of such rubbers we used SKB, SKV, DB-2 and SKBM. Figure 6 gives the results of measurements made on mixtures of SKS-30 with these polybutadiene rubbers, and also with SKS-10. The figure shows that the anomaly of the systems SKS-30 + SKB is characteristic of any combination of SKS-30 with polybutadiene rubbers, but is not seen in combinations of any two butadiene-styrene rubbers (SKS-30 + SKS-10). Further testing of the properties of rubbers prepared on a base of a combination of different polybutadiene rubbers with one another also failed to reveal any such anomaly in stocks of the same type.

Thus, rubbers of the same type when mixed together exhibit no such basic change in the properties of the stocks as are obtained from mixtures of butadiene-styrene rubber with polybutadiene rubber. Since the anomaly noted is not observed in mixtures of rubbers of the same type, but is clearly exhibited in many cases where a polar rubber is mixed with a nonpolar one, it is logical to assume that this anomaly is related to the mutual solubility of the mixed rubbers. A good mutual solubility facilitates the formation of true solutions of one polymer in the other, which results in a steady change in the properties

as the proportions of the rubbers change. In the case of limited mutual solubility of the polymers, however, rubbers mixed by force on the mill rolls cannot separate into two phases in macroscopic amounts by reason of the prohibitively high viscosity of the uncured stocks, but instead these separate into phases only in extremely small volumes. The micrononhomogeneous uncured rubber stock which is obtained becomes fixed in this condition during vulcanization. One characteristic of the structure of such micrononhomogeneous stocks is also revealed, in our opinion, by the anomalous properties pointed out above. From this viewpoint it is easy to understand (as being the result of the non-
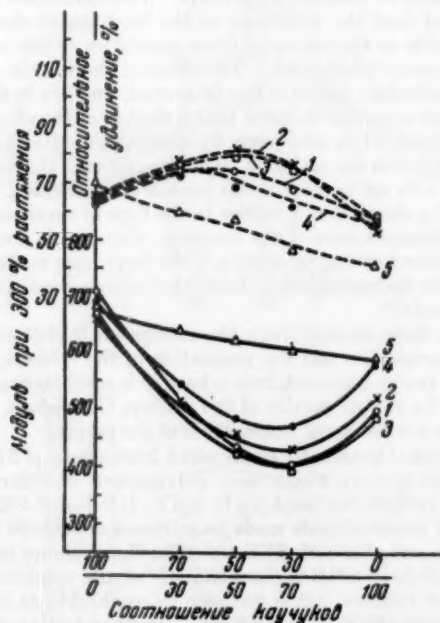
Fig. 6.—Mechanical properties of cured stocks containing mixtures of SKS-30 with different polybutadiene rubbers and with SKS-10. *1*—SKBM; *2*—DB-2; *3*—SKV; *4*—SKB; *5*—SKS-10. Solid line—per cent elongation at break; broken line—modulus at 300% elongation. The abscissa represents the proportion of the rubbers in per cent; the outer ordinate represents the modulus at 300% elongation, the inner one the per cent elongation at break.

homogeneous distribution of stresses and deformations in micrononhomogeneous stocks of this type) the decrease in tensile strength, in the per cent elongation at break and in dynamic flex life, as well as the increase in the elastic properties.

The size of the nonhomogeneous portions should be very small because of the fact that the microregions of different composition (the different phases) are found to be connected together, forming a whole, by long chain molecules which pass through several such regions. Evidently this is the special feature of the mixing of two polymers which are mutually soluble to only a limited degree.

From our data it must be concluded that SKB and SKS-30 when combined in one stock give a micrononhomogeneous stock. A detailed consideration of

this unexpected conclusion, based on further physico-chemical testing, will be given in subsequent reports[7].

In conclusion it must be emphasized that even polymers with good mutual solubility can be prepared in the form of a nonhomogeneous system if the mixing is not done carefully enough, while polymers of limited solubility may become fixed (e.g., by vulcanization in the case of rubber) in some nonequilibrium condition of the raw stock. Hence it is to be expected that through some special processing one would probably be able to create or remove the anomalies which we have observed in the properties of combined cured stocks. From our viewpoint it is important that such combined stocks, prepared under conditions where a thermodynamic equilibrium is achieved (in microregions) do in fact display the distinctive properties described above, which are related to their mutual solubility and to the chain structure of the molecules. This should be taken into consideration both in the practical applications of mixed polymers and in the theoretical study of solutions of one polymer in another.

CONCLUSIONS

1. The mixing of rubbers (or of any amorphous polymers) may be considered as a mutual solution of two liquid phases, conforming to thermodynamic laws.

2. The stocks studied, which were prepared from a base of a combination of different rubbers, fall into two groups as regards the nature of the relation between their mechanical properties and the proportions of the mixed rubbers. The opinion was expressed that the anomalies observed in the properties of combined stocks prepared from a mixture of SKS-30 and SKB are due to the micrononhomogeneous two-phase structure of such stocks.

3. It was shown that the properties of combined stocks are governed primarily by the behavior of the mixed rubbers themselves, and not by the ingredients incorporated into the stocks.

4. The compatibility of two polymers should be considered from two points of view. A macroscopic compatibility can almost always be achieved, provided that the polymer can be converted to the fluid state. However, compatibility in microregions, i.e., the mutual solubility of polymers, is determined by their thermodynamic properties and may not coincide with macrocompatibility. The reason for the discrepancy between macro- and microcompatibility is the chain structure of the polymer molecules, and the resulting large viscosity of polymers which have a high mobility of small segments of the flexible chain molecules.

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[7] The formation of stable bonds between the chemical groups of different molecules of two mixed polymers might explain the anomaly of mechanical properties which we have observed. However, this explanation conflicts with the fall in tensile strength in the combined stocks, and does not agree with the behavior of mixtures of solutions of the corresponding polymers. Furthermore, for the systems we have considered there is no basis for such a hypothesis.

MASTICATION. V. SEPARATION AND STRUCTURAL INVESTIGATION OF NATURAL RUBBER-POLYMETHYL METHACRYLATE INTERPOLYMERS FORMED BY MASTICATION *

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Polymers in a rubbery state are frequently milled or masticated in an internal mixer to admix other materials and/or to degrade the polymer. The degradative reaction is mechanically induced rupture of the polymer molecules to free radicals[1,2]. In the absence of oxygen and other terminating compounds, these radicals initiate the polymerization of monomers incorporated in the rubber[3]. The products formed by masticating the system, natural rubber-methyl methacrylate, have been examined in order to determine the structure of the interpolymer and the factors controlling its yield and segmental lengths.

EXPERIMENTAL

Materials.—The natural rubber was acetone-extracted deproteinized crepe[3] of limiting viscosity number, $[\eta]$, of 385 ml g^{-1} benzene. Methyl methacrylate (Kallodoc of I. C. I. Ltd.) was washed with 10 per cent aqueous sodium hydroxide and distilled water and dried over sodium sulfate.

Mastication.—The small laboratory masticator and the handling of the rubber-monomer and rubber-polymer mixtures have been described previously[3,4].

Osmotic molecular weight measurements.—Number average molecular weights were obtained from osmotic pressures of benzene solutions recorded in Zimm-Meyerson Osmometers[5] fitted with Ultra-cella-filter finest-grade membranes (Membranfiltergesellschaft, Göttingen). Duplicate osmotic pressures for at least three concentrations in the range 0.2–1.0 g/100 g benzene were made and occasionally checked in different osomometers.

Linear π/c *versus* c curves were obtained with the homo- and interpolymers, from which μ values[6] for the latter were calculated from the formulas:

$$\pi/c = RT(A + Bc) \quad \text{and} \quad B = (\tfrac{1}{2} - \mu)(w_a v_a + w_b v_b)^2 V_1^{-1}$$

where w_a, w_b, and v_a, v_b are the weight fractions and specific volumes, respectively, of the two polymeric components of the interpolymer and V_1 is the molar volume of benzene.

Limiting viscosities in benzene solution were determined by conventional means[2]. The relationship $M_n = 2.81 \times 10^5 [\eta]^{1.32}$ was employed to give values of number average molecular weight for the unfractionated polymethyl meth-

acrylate[7]; the osmotic molecular weight of a sample of uncombined plastomer after mastication, 275,000 and its limiting viscosity number, 95 ml g^{-1}, were in agreement with this relationship. The relationship $[\eta] = 5.55 \times 10^{-6} \, M^{1.05}$ for unfractionated masticated rubber[8] was employed to give approximate molecular weight values for the uncombined rubber and free rubber produced by autoxidation of the interpolymer.

Ozonolysis (in collaboration with Dr. D. Barnard[9]).—The rubber segments but not the plastomer from interpolymer were ozonized by using little more than the theoretical quantity of ozone for the rubber and adding di-n-butyl sulfide as a material of intermediate reactivity with ozone to protect the plastomer. Isolation of about 90 per cent of the polymethyl methacrylate was
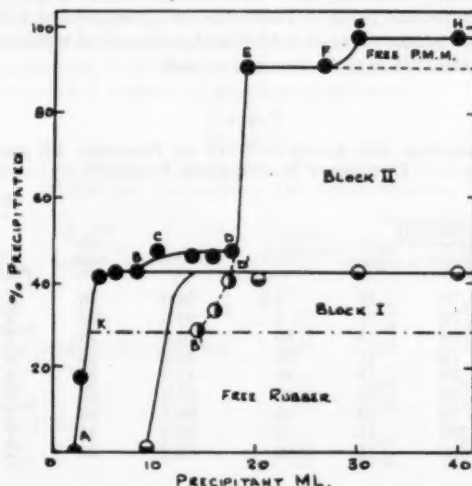
Fig. 1.—Separation of the polymeric products obtained after masticating natural rubber containing 38.5% methyl methacrylate to 97% conversion; (●) fractional precipitation by methanol from 10 ml of 1% benzene solutions; (◑) fractional precipitation by acetone; (◐) fractional precipitation by methanol after removal of free rubber; (---) fraction extracted by petroleum ether.

achieved, but as the fraction which was not precipitated was of low molecular weight, the viscosity-molecular weight relationship used gave an overestimate of the lengths of the original plastomer.

Autoxidation.—0.5 g/100 ml of isolated interpolymer was maintained at 60° C in benzene with bubbling of oxygen for 4–8 hours. The benzene was evaporated off under reduced pressure and the dried polymer suspended in petroleum ether to extract the free rubber produced by oxidative scission. The weight fractions and viscosities of the free rubber were measured.

RESULTS

Separation of uncombined polymers and interpolymer.—Fractional precipitations of 1 per cent solutions of degraded natural rubber and polymethyl methacrylate in benzene by methanol gave quantitative separation to within 2 per cent of the polymers, with a wide gap in titer between the end of the rubber precipitation and the onset of the polymethyl methacrylate precipitation[10]. Com-

plications, however, arose on attempting to separate similarly the products of mastication, a typical precipitation curve for which is given in Figure 1. No precipitate settled out up to point D without centrifuging, and reproducible amounts of precipitate required centrifuging at 20,000 g for >10 minutes. From the onset of precipitation, the solution became progressively more turbid until coagulation at E, the same solvent composition as reported for coagulating natural rubber-polymethyl methacrylate graft polymer[10]. A further fraction FG precipitated after a distinct gap in titer of clear solution EF. The fractions precipitated were reproducible to within ±3 per cent for separately masticated samples.

Elemental and infrared analyses showed the third fraction FG to be >98 per cent polymethyl methacrylate. The second fraction BE, which precipitated in the intermediate range between the two polymers of a simple mixture, contained different proportions of rubber and polymethyl methacrylate depending upon the masticated sample being analyzed.

TABLE I

SEPARATION AND ANALYSIS DATA OF FRACTION AB FROM
DIFFERENT MASTICATION PRODUCTS

Milling conditions					Wt. % AB/ total wt.	Fraction AB	
% monomer	Speed, rpm	Temp., °C	Time, min	Conversion, %		% PMM	% uncombined rubber
23.8	76	15	2.5	46.0	76	3	82
23.8	76	15	5	90.3	60	5	67
38.5	76	15	10	96.2	38	7	71
48.5	76	15	20	93.2	40	8	72
55.4	76	15	40	17.9	78	4	84
38.5	76	25	15	97.0	42	8	79
38.5	76	35	35	98.7	42	7	73
38.5	360	15	15	98.4	46	7	75
55.4	360	15	80	98.2	35	5	86

The first fraction AB also contained significant proportions of polymethyl methacrylate (Table I) and so could obviously not be taken as a satisfactory separation of free rubber, as might have been suggested by precipitation of the uncombined polymers and the three steps in the precipitation curve of Figure 1. Acetone as precipitant gave the same content and composition of the fraction precipitated. The same fraction was precipitated by acetone from toluene and pyridine as from benzene solution.

A few per cent of polymer could be centrifuged out of the sol between the first and second fractions (Figure 1). Though only little outside experimental error, the slight increase in precipitate was shown to be real by a change from a transparent film on drying down the sol at B to an opaque film on drying down the sol at C. This increment of precipitation is later included as part of the second fraction BE.

Similar results were obtained on attempting to precipitate only free polymethyl methacrylate from benzene solutions by petroleum ether. Precipitation was quantitative from simple mixture with rubber, but included a rubber component from masticated mixtures.

Simple extraction procedures overcame the inadequacies of fractional precipitation. Suspension in 60–80° b.p. petroleum ether and acetone leached

out pure rubber and polymethyl methacrylate, respectively, from the products of mastication and petroleum ether extracted the same amount of rubber AK from the fraction AB of Figure 1 as from the whole product. The quantity of polymer extracted reached a constant value after 4 days at room temperature. The free rubber content increased slowly on longer standing and raising the temperature of undegassed solutions but remained constant for degassed solutions.

To test that free rubber and polymethyl methacrylate were completely extracted from the masticated mixtures, different proportions of rubber of high molecular weight and polymethyl methacrylate (A) were blended with portions of a masticated sample (B). The mixtures were suspended in petroleum ether and acetone and precipitated from benzene solution by methanol and acetone. The increase in extracts and in fraction 1 precipitated corresponded closely with the amounts of free polymers added (Table II). It is concluded, in particular, from these results that extraction by petroleum ether provides the free rubber content of masticated samples.

TABLE II

SEPARATION OF ADDED RUBBER AND POLYMETHYL METHACRYLATE (PMM) BY EXTRACTION AND PRECIPITATION

System	Rubber extracted, %	Fractional ppt		PMM extracted, %
		By methanol	By acetone	
Mixture (A)				
Observed	51	51	51	45
Calculated	54	54	54	46
Mastication product (B), observed	30	42	42	10
Blend 2(A):1(B)				
Observed	44	50	48	36
Calculated	46	50	50	34
Blend 1(A):1(B)				
Observed	43	49	47	30
Calculated	42	48	48	28

After extraction of the free polymers, fractional precipitation by methanol gave turbid solutions but no precipitation on centrifuging up to B' and then coagulation according to the curve B'D'E of Figure 1. The precipitate B'E gave no extract on suspension in petroleum ether and acetone. Addition of acetone or petroleum ether instead of methanol gave turbid solutions but no precipitation. When the extracted rubber was redissolved in a benzene solution of precipitate B'E, the original curve A-E was obtained, but only on centrifuging, and acetone also gave precipitation to the BD' level. Likewise, precipitation of the rubber-containing component by petroleum ether did not occur unless free polymethyl methacrylate was present. Thus the complications of fractional precipitation of the free polymers and interpolymer were caused by their cosolvation and coprecipitation.

(The fractional precipitation of other systems indicate that these complications generally occur with polymer-interpolymer mixtures. For example, polymethyl methacrylate-styrene mixtures and interpolymer prepared by the method of Smets and Claesen[11] and by a mastication technique gave only ill-defined fractions on precipitating from benzene by methanol. More distinct fractionation occurred on stepwise precipitation and centrifuging. Clearly separated free polymer and interpolymer fractions were obtained by stepwise

precipitation and centrifuging from the poorer solvents 1:1 chlorobenzene:benzene or 1:1 acetone:benzene by petroleum ether or methanol, respectively.)

The methods of separation available allow isolation of the whole of the interpolymer by extraction of the free polymers, or its separation into two fractions by precipitation of fraction 1 and extraction of free rubber and "block I" interpolymer, and fraction 2 as a second interpolymeric "block II" fraction (Figure
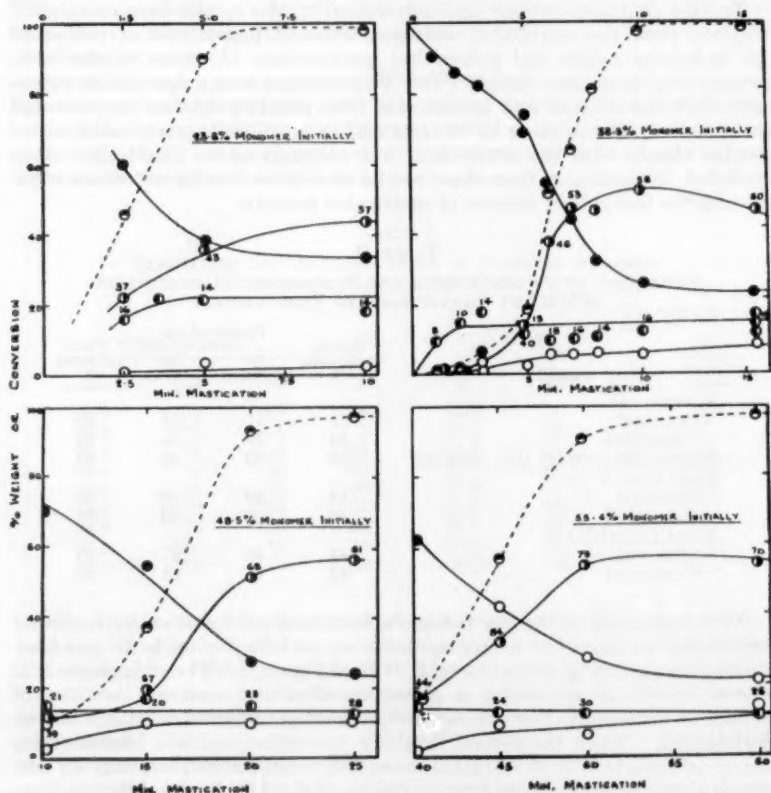
Fig. 2.—Analysis of products at various extents of polymerization :(●) extent of polymerization; (●) free rubber; (◐) block I (the numbers refer to the percentage of PMM in the samples); (◑) block II; (○) free PMM.

1).   The importance of these alternative separation procedures lies in the opportunity to cross check the content of fractions by two methods, for example, free polymethyl methacrylate by acetone extraction and methanol precipitation, block II by methanol precipitation and acetone extraction followed by acetone precipitation, etc.   Cross-checking of fractions from 34 separations covering the range of conditions employed gave equal contents of fractions within the 1–2 per cent error of each of the methods.

The method employed depended on the objective.   Although no very sharp

or fundamental distinction between block I and II is envisaged, block I is rubber-rich compared with block II (86 and 58 per cent rubber, respectively, in the sample of Figure 1). On varying the conditions of reaction, the yield and structure of these two interpolymer fractions provide insight into the mechanism.

Variation of monomer concentration.—Analyses of the products after mastication of rubber with different initial monomer concentrations are summarized in Figure 2. The longer induction periods with greater amounts of monomer are attributable to lower rates of initiation by shear of the softer mixtures[3]. During the early stages, the plastomer formed mainly the block I interpolymer. The yield of the block II interpolymer increased rapidly during the period of rapid polymerization and decreased slightly near complete conversion. The most significant change in the relative amounts of fractionated components with increased initial monomer concentration is the increase in the block II fraction.

TABLE III

THREE-STAGE POLYMERIZATION OF METHYL METHACRYLATE BY MASTICATION WITH NATURAL RUBBER AND EFFECT OF MOLECULAR WEIGHT OF RUBBER ON COMPOSITION OF PRODUCTS

| | | | | Fraction analysis | | | |
System	Stage	Time, min	Conversion, %	Free rubber	Block I	Block II	Free PMM
(A) Undegraded rubber	1	10	95.4	37	17	29	18
	2	8	96.7	27	13	61	47
	3	7	100	25	6	78	103
(B) 50% Undegraded rubber +50% Degraded rubber	1	17	94.7	45	9	32	12
	2	15	95.1	37	3	81	30
	3	10	100	33	2	105	77
Fractionated rubber							
$[\eta]$ = 428	1	9	98.3	26	21	36	12
$[\eta]$ = 461	1	8	95.5	22	26	38	11

Successive addition of monomer.—As at least one-third of the rubber remained non-interpolymeric after a single batch polymerization, three-stage polymerization was carried out to ascertain if there was a lower limit to the amount of rubber uncombined and to compare the proportions of the other fractions. (Masticating scrol s of a different pattern to those otherwise employed enabled mastication of the unusually hard products.) The undegraded rubber (A) of Table III was of $[\eta]$ = 385 ml g^{-1} and (B) was a 50 per cent mixture with degraded rubber of $[\eta]$ = 110 ml g^{-1}. After the first stage of polymerization of 2 ml monomer in 3 g rubber, 3 g of the product reimbibed a further 2 ml monomer and was masticated to almost complete polymerization. The third stage was carried out similarly.

In the presentation of the results (Table III), the experimental values of the weight fractions at stages 2 and 3 have been scaled up to those for the whole sample by dividing by the fraction of the products taken for the mastication. The amount of rubber uncombined tended to a limiting value. The block I fraction decreased almost to zero and became richer in polymethyl methacrylate, and the fractions of block II and free plastomer increased during the three-stage polymerization.

Effect of molecular weight of the rubber.—Using rubbers (A) and (B) of

Table III, less uncombined rubber in the products occurred with the initial rubber of higher average molecular weight. This trend was confirmed by single-stage polymerizations using rubber of higher molecular weight obtained by precipitating 79 and 52 per cent of undegraded rubber from benzene by slow addition of methanol (Table III).

Effect of temperature.—The only significant variation caused by a change in temperature of reaction from 15 to 35° C was in the period of reaction for a given extent of polymerization; 95 per cent conversion required 10, 14, and 35 min at 15, 25, and 35° C, respectively, for an initial mixture of 38.5 per cent
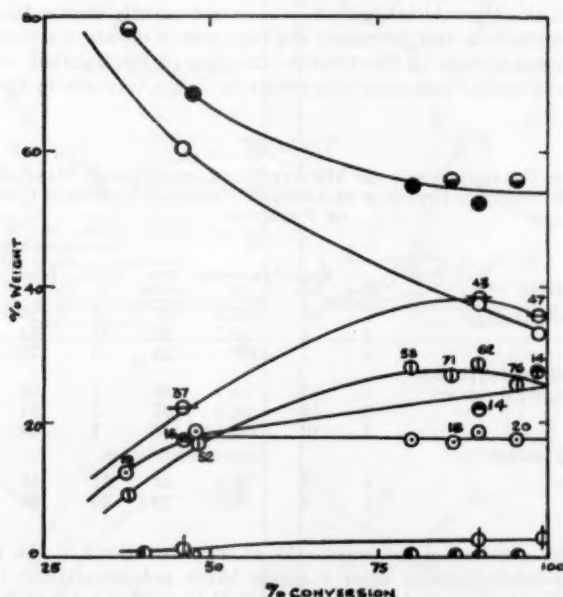
Fig. 3.—Influence of solvents in the composition of the polymerized products after mastication: free rubber without solvent (○), with benzene (◐), with carbon tetrachloride (●); block I without (◓) and with solvent (◉); block II without (⊖) and with solvent (⊘); free PMM without (◔) and with solvent (◖). The numbers refer to the PMM content of the samples.

monomer in rubber[3]. A small increase in the minimum of free rubber at about 95 per cent conversion was noted with increase in temperature—25, 30, and 33 per cent for the above experiments.

Effect of solvent dilution.—Addition of solvent retarded the reaction[3]. The products after different extents of conversion of 1 ml methyl methacrylate in 3 g rubber are compared in Figure 3 with those of 1 ml monomer and 1 ml of benzene or carbon tetrachloride. The nature of the solvent had little effect. Its addition increased the amount of uncombined rubber, reduced block I and increased its plastomer content slightly, decreased block II and increased its plastomer content, and reduced to zero the free polymethyl methacrylate.

Effect of transfer agent.—The presence of *tert*-dodecyl mercaptan reduced the rate of conversion (Figure 4). The mercaptan increased the free rubber
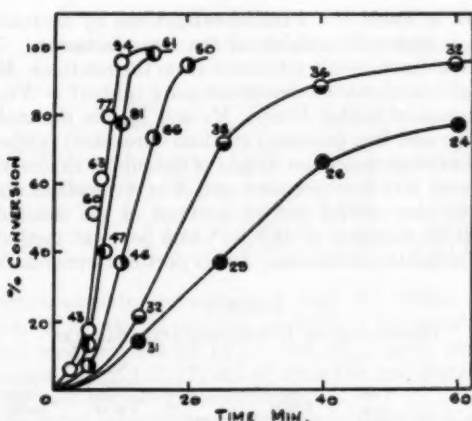
Fig. 4.—Effect of transfer agent on polymerization rate of initially 38.5% methyl methacrylate in natural rubber. 0, 0.2, 0.5, 2.0, and 5.0 ml *tert*-dodecyl mercaptan per 100 ml monomer, respectively. The numbers in the figure are the viscosities of the polymeric products measured on the Wallace Rapid Plastimeter[13].

and polymethyl methacrylate content and reduced their viscosities, tended to increase block I content, and markedly reduced that of the block II fraction (Table IV).

Ozonolysis.—After almost complete polymerization of monomer in rubber at different concentrations and different extents of conversion for one concentration, the products were ozonized to remove all the rubber. The recovery of polymethyl methacrylate and its molecular weight from the viscosity relation-

TABLE IV

ANALYSIS AFTER MASTICATION OF INITIALLY 38.5% METHYL METHACRYLATE
IN NATURAL RUBBER IN THE PRESENCE OF *tert*-DODECYL MERCAPTAN

Transfer agent, %	Time, min	Conversion, %	Fraction analysis				Free rubber $\bar{M}_n \times 10^{-3}$	Free PMM $\bar{M} \times 10^{-6}$
			Free rubber	Block I	Block II	Free PMM		
0	5	17.2	73	11	8	1		
	6	51.5	51	9	36	5		
	7	62.6	43	7	42	8		
	8	79.7	36	9	46	8		
	10	96.2	26	14	49	10	1.90	2.80
0.2	5	13.2	78	7	11	2		
	7.5	40.6	63	6	25	6		
	10	77.7	40	14	37	9		
	15	97.7	24	18	45	13	1.30	2.60
0.5	10	36.7	69	3	23	5		
	15	74.3	42	14	27	17		
	20	94.5	31	20	28	20	1.13	2.20
2.0	12.5	21.2	78	9	6	6		
	25	73.7	54	9	19	18		
	40	87.7	46	17	16	21		
	60	95.7	38	23	16	23	1.10	1.05
5.0	12.5	15.2	79	5	9	7		
	25	37.2	64	16	8	12		
	40	67.0	59	17	4	20		
	60	77.5	52	17	6	25	0.74	0.50

ship are recorded in Table V. Parallel extractions by acetone and viscosity measurement gave molecular weights of the free plastomer. The number of rubber chains cut at least once is estimated from the relations, $M_b = \{M_0 - (1 - w_b)M_f\}/w_b$ and (no. of rubber chains cut per g rubber) $= Nw_b/M_b$, where w_b is the weight fraction of rubber bound, M_0 and M_f are the molecular weights of the initial rubber and free (assumed residual unreacted) rubber, respectively, M_b is the original average molecular weight of the rubber chains which have been degraded and bound into interpolymer, and N is Avogadro's number.

Ozonolysis was also carried out on portions of the isolated interpolymer fractions from initial mixtures of 23.8 and 38.5 per cent methyl methacrylate taken to almost complete conversion. Other portions were reserved for osmotic

TABLE V
OZONOLYSIS OF UNFRACTIONATED SAMPLES

Monomer, %	Time, min	Conversion, %	% PMM recovered	PMM $M_n \times 10^{-5}$	No. interpolymer PMM chains $\times 10^{-16}$	No. rubber chains cut $\times 10^{-16}$	Free PMM $M_n \times 10^{-5}$
23.8	7.5	98.0	68	1.35	3.54	3.83	0.85
38.5	5	28.4	95	2.40	1.19	1.38	—
	6	35.1	94	4.85	0.81	1.71	—
	7	55.5	95	4.30	1.53	2.71	—
	10	97.8	81	3.45	2.64	4.26	3.10
48.5	25	94.5	97	4.60	2.40	3.53	4.60
55.4	60	94.0	94	6.60	2.46	3.62	5.25

molecular weight determination. The essential difference between the block I and II fractions is the greater length of rubber segments and shorter length of plastomer segments in the former (Table VI).

Autoxidation.—Interploymer fractions were separated after monomer at three concentrations had been polymerized. The rubber components were subjected to autoxidation. The weight fractions and molecular weights of the free rubber produced are given in Table VII.

Milling of rubber-polymethyl methacrylate mixtures and interpolymers.—A mixture of rubber and polymethyl methacrylate was prepared by shock-precipitating a benzene solution into methanol and drying. On milling in air on a 6 inch diameter laboratory mill with 1 per cent thiophenol added to ensure

TABLE VI
OSMOTIC MOLECULAR WEIGHTS, VISCOSITIES, AND OZONOLYSES OF ISOLATED INTERPOLYMERS

System	Ozonolysis % PMM recovered	Ozonolysis PMM $M_n \times 10^{-5}$	Total interpolymer $M_n \times 10^{-5}$	μ	$[\eta]$	k'
23.8% MM, 90% conversion						
Block I	72	1.10	4.50	0.43	355	0.35
Block II	87	2.00	4.00	0.47	220	0.26
38.5% MM, 97% conversion						
Block I	86	1.10	5.10	0.43	345	0.47
Block II (a)	85	2.80	5.70	0.44	252	0.28
(b)	81	3.25	—	—	—	—
Blocks I + II	—	—	5.65	0.44	—	—

TABLE VII
AUTOXIDATION OF INTERPOLYMER FRACTIONS

| System | Block fraction | Resulting free rubber | | | Original free rubber |
		w_f	$\bar{M}_n \times 10^{-4}$	$\alpha \times 10^2$	$\bar{M}_n \times 10^{-4}$
23.8% MM, 90% conv.	I	0.59	0.86	1.00	1.83
	I + II	0.48	1.00	0.72	
38.5% MM, 97% conv.	I	0.39	1.71	0.34	
	II	0.45	0.84	0.78	1.78
	I + II	0.16	1.46	0.16	
55.4% MM, 94% conv.	I + II	0.12	1.35	0.13	1.79

predominant radical-acceptor termination[1], only the rubber component was degraded. Thus, 75, 50, and 25 per cent mixtures of rubber of $[\eta] = 385$ ml/g with polymethyl methacrylate of $[\eta] = 550$ ml/g gave, after milling and separating, rubber of $[\eta] = 157, 72$, and 38 ml/g and polymethyl methacrylate of $[\eta] = 554, 540$, and 555 ml/g, respectively.

When the separated interpolymer from the initially 38.5 per cent methyl methacrylate system was similarly passed through the mill, both free rubber and free polymethyl methacrylate were formed in significant amounts (Table VIII).

STATISTICAL ANALYSIS OF INTERPOLYMER STRUCTURE

Experimental methods of completely isolating the free polymer and interpolymer fractions and of measuring the lengths of attached segments of the interpolymer (for example, polymethyl methacrylate segments by ozonolysis of rubber segments) are not always available. It is, however, often possible to isolate and measure the weight fractions and molecular weights of one or more

TABLE VIII
DEGRADATION OF ISOLATED INTERPOLYMER BY MASTICATION WITH 1% THIOPHENOL

No. passes through mill	0	10	20	35	50	80
% free rubber	0	52	66	75	83	89
% free PMM	0	17	26	34	38	43

fractions and carry out further reactions. Simple statistical treatment of the results may then give considerable information on the structure of the interpolymer. The part of the statistical treatment given below illustrates the method and is later applied to the data on isolating free rubber after mastication and on autoxidation of the rubber in the isolated interpolymer.

Free rubber after reaction.—It is assumed that the initial rubber molecules have a random distribution of chain lengths[12] given by $N_x/N = \beta_0 \exp\{-\beta_0 x\}$, where $1/\beta_0$ is the number average molecular weight, N_x is the number of mole-cules of length x monomeric units, and $N = \sum_{1}^{\infty} N_x \approx \int_{0}^{\infty} N_x dx$. Let α_0 be the fraction of the initial links between units which are ruptured, all units assumed to have an equal probability of rupture. (These two assumptions are probably only crude approximations for the system under investigation[8,17], but are likely to be close approximations for selected random grafting by normal chemical reaction.)

The number of monomer units in chains of length t which have not been ruptured is[13]:

$$tN_t^0 = tN_t(1 - \alpha_0)^t \approx N\beta_0 t \exp\{- (\alpha_0 + \beta_0)t\} \tag{1}$$

Integrating from $t = 0$ to ∞ and dividing by the total number of monomer units, N/β_0, gives the weight fraction of free rubber as:

$$w = \beta_0^2/(\beta_0 + \alpha_0)^2 \tag{2}$$

The chain length of the free rubber is:

$$\nu = 1/(\alpha_0 + \beta_0) \tag{3}$$

Similar arguments give the number of rubber segments possessing one end formed by rupture, N', and of rubber segments possessing two ends formed by rupture, N'', as:

$$N' = 2\alpha_0 N/(\alpha_0 + \beta_0) \quad \text{and} \quad N'' = \alpha_0^2 N/\{\beta_0(\alpha_0 + \beta_0)\} \tag{4}$$

The fractions $q = N'/(N' + N'')$ and $(1 - q) = N''/(N' + N'')$ are then given by:

$$q = 2\beta_0/(2\beta_0 + \alpha_0) \quad \text{and} \quad 1 - q = \alpha_0/(2\beta_0 + \alpha_0) \tag{5}$$

The value of α_0 is determined from the known w and β_0 by (2) and then the fractions of rubber chains attached at one and both ends to polymethyl methacrylate by (5).

Random scission of rubber in isolated interpolymer.—Let the rubber segments of the isolated interpolymer be of random chain length around the mean value $1/\beta$ and random degradation occur to extent α.

(A) For interpolymer with all rubber segments joined at only one end to polymethyl methacrylate segments and of random distribution, the weight and chain length are readily deduced[13]:

$$w = \alpha/(\alpha + \beta) \quad \text{and} \quad \nu = 1/(\alpha + \beta) \tag{6}$$

Similarly the chain length of the rubber both bound and free is given by (6); hence the molecular weight of the free segments is equal to that of the bound.

Likewise for interpolymer with all the rubber segments joined at both ends to polymethyl methacrylate segments and of random distribution:

$$w = \alpha^2/(\alpha + \beta)^2 \quad \text{and} \quad \nu = 1/(\alpha + \beta) \tag{7}$$

(B) For interpolymer with a fraction q of rubber segments joined at one end:

$$w = q\frac{\alpha}{\alpha + \beta} + (1 - q)\frac{\alpha^2}{(\alpha + \beta)^2} \quad \text{and} \quad \nu = 1/(\alpha + \beta) \tag{8}$$

i.e.,

$$w = \alpha\nu\{q + (1 - q)\alpha\nu\} \tag{9}$$

(*C*) For the case of random rupture of initially uniform rubber segments of length x:

$$w = 1 - (1 - \exp\{-\alpha x\})/\alpha x$$

and

$$\nu = \{1 - (1 - \exp\{-\alpha x\})/\alpha x\}/\alpha \tag{10}$$

(*D*) To approximate more closely to the distribution of rubber segment lengths of the interpolymer formed by mechanical rupture[17], let their distribution be:

$$N_x = N\beta(1 - \beta)^{x-x_0} \approx N\beta \exp\{\beta(x - x_0)\} \tag{11}$$

where $x > x_0$ and $2x_0$ is the critical length of rubber molecules below which scission does not take place. Random autoxidative scission to extent α gives:

$$w = \frac{1}{x_0 + 1/\beta}\left[x_0 + 1/\beta - 1/\alpha + \frac{\beta \exp\{-\alpha x_0\}}{\alpha(\alpha + \beta)}\right] \quad \text{and} \quad \nu = x_0 + 1/\beta \tag{12}$$

From (4) to (12), the values of β or x can be derived from weight fractions and molecular weights of free rubber for different proposed interpolymer mechanisms.

DISCUSSION

Course of the reaction.—During the initial stage of slow polymerization, the interpolymer formed is largely of the block I type (Figures 1 and 2), which composition, molecular weight determination, and ozonolysis reveal to be composed of relatively long rubber segments and short plastomer segments. This is consistent with preferential rupture of the longer rubber molecules and growth of plastomer chains less influenced by the Trommsdorff gel effect[14,15] than at later extents of reaction. The block I fraction is only isolated from solutions as a coprecipitate with free rubber on centrifuging because of the interaction of its long rubber segments with free rubber molecules.

During the period of rapid polymerization, greater proportions of the block II than of the block I interpolymer are formed. The block II fraction possesses shorter rubber segments and longer plastomer segments than the block I interpolymer. The rate of initiation increases with extent of conversion and attendant increase in bulk viscosity. This increase in initiation rate is insufficient to offset the increase in molecular weight of the polymer attributable to the decreased termination rate by the gel effect. At high extents of reaction, however, the molecular weight of the polymer formed again decreases, as expected from a decrease in propagation rate by monomer depletion or reduction in propagation rate constant[16] while the rate of initiation is still increasing. The experimental separation into distinct block I and II fractions is a consequence of the sudden onset of the gel effect.

On approaching complete conversion after mastication with different initial monomer concentrations and successive stepwise polymerization, the fraction of the rubber not in the interpolymer is appreciable and approximately constant. Its fraction is higher with initial rubber of lower molecular weight. Superficially these results suggest that the stage of rubber degradation has been reached when the only rubber molecules remaining uncombined are those not subject to scission by the applied shearing forces. Such a view of a molecular weight below which scission by shear is inoperative has experimental and

theoretical support[17] and explains the viscosity-molecular weight relationship of rubber after various extents of cold mastication[8] and the leveling off of the molecular weight at 70,000 to 100,000 on continued mastication. However, the widely differing shear conditions with different initial amounts of monomer in the present case would be expected to lead to different proportions of free rubber with molecular weight considerably lower than the experimental values of almost 200,000. Again, the free rubber isolated after complete polymerization can initiate the polymerization of further methyl methacrylate on mastication and is therefore clearly capable of further rupture. The free rubber therefore seems to arise in part from incomplete degradation of the original rubber molecules and in part from shear of the interpolymer.

In conjunction with the result that free rubber and free polymethyl methacrylate are produced on milling the isolated interpolymer, it seems necessary to advance especially facile rupture near the link joining already formed rubber and plastomer segments during polymerization.

In accordance with its transfer reactivity, *tert*-dodecyl mercaptan markedly increased the amounts of uncombined polymethyl methacrylate. It also retarded the rate of polymerization due to the remarkable softening rather than hardening of the mixture during polymerization as well as a reduction of the Trommsdorff gel effect. The high yields of free rubber are explicable by a direct transfer reaction between mercaptan and the initiating rubber radicals.

Structure of the interpolymer.—The following observations favor a linear block rather than a branched graft structure for the interpolymer: (*1*) Rupture occurs in the backbone of the rubber molecules and methyl methacrylate in small amounts behaves as a noncrosslinking radical acceptor[3]. (*2*) The values of the viscosity and osmotic interaction constants, k' and μ, respectively, are intermediate between those of the homopolymers, whereas substantially higher values of k' have been found on preparing graft polymer. (*3*) A grafting reaction would require a hydrogen-transfer reaction between polymer radical and rubber molecule, which is absent during normal catalytic polymerization of methyl methacrylate in the presence of rubber[10]. (*4*) A grafting reaction, not being so dependent on molecular weight of rubber molecules as the primary mechanical scission, would give decreasing amounts of free rubber after each stage of polymerization.

The molecular weight data for the two samples of rubber-polymethyl methacrylate analyzed in most detail are summarized in Table IX. The osmotic molecular weight and composition of the interpolymer and molecular weight of the polymethyl methacrylate determined after ozonolysis indicate that the interpolymer molecule contains one plastomer segment.

The lengths of the rubber segments have to be deduced from the less direct autoxidation results. These deductions suffer from the present uncertainties of chain length distribution. This in turn is partly based on only approximate knowledge of the mechanical rupture of a link between monomeric units depending on its position in the chain and chain length of the rubber molecule. The several cases treated in the statistical section, probably bracketing the true distribution, give the lengths of the rubber segments of Table IX. One to two rubber segments per interpolymer molecule are found for these different distributions.

The molecular weight of the free rubber also indicates the chain lengths of the bound rubber segments; for random scission, the molecular weight of the free rubber is equal to that of the bound segments. The measured molecular

TABLE IX

System	Block fraction	Over-all MW ×10⁻³	Cal.* segmental MW ×10⁻³		Ozonolysis $\bar{M}_n$ PMM ×10⁻⁴	Autoxidation $\bar{M}_{n,\text{Rubber}}$ ×10⁻³				$\bar{M}_n$ ×10⁻³	
			Rubber	PMM		A	B	C	D	Free rubber	Free PMM
38.5%, milled 10 min, 97% conv.	I	5.10	4.40	0.70	1.10	2.80	3.03	4.80	2.84		
	II	5.70	3.30	2.40	3.00	1.50	2.10	2.48	—		
	I + II	5.65	—	—	2.85	1.86	1.82	3.29	—	1.80	2.75
23.8% MM, milled 5 min, 90% conv.	I	4.50	3.60	0.90	1.10	2.10	3.32	3.16	—		
	II	4.00	2.50	1.50	2.00	1.50	2.16	—	—		
	I + II	—	—	—	1.35	1.91	1.82	3.10	—	1.80	0.83

* Assuming one segment of each component per interpolymer molecule. The rubber values will be halved if termination by combination or crossed termination is predominant.

A, B, C, and D refer to the several cases discussed in the section on statistical methods. The value of X_0 in D is taken as 500.

weight of the free rubber and total chain length of bound rubber from molecular weights and composition of the interpolymers is consistent with two rubber segments per interpolymer molecule.

The number of rubber segments per polymethyl methacrylate segment might be predictable if the mode of termination of polymethyl methacrylate radicals was established. Unfortunately, the termination process has not been unambiguously determined, although there seems general agreement that combination is significant at higher temperatures than those employed here and that the proportion of radicals undergoing combination is increased by lowering of temperature. There is also the possibility that termination may occur by a facile reaction between polymethyl methacrylate and some of the polyisoprenyl radicals produced by shear. On balance, therefore, the interpolymer molecule is more probably composed of a plastomer segment between two rubber segments rather than only one segment of each polymer.

SUMMARY

Polymerization of methyl methacrylate admixed with natural rubber occurs on rupture of rubber molecules to free radicals by applied shearing forces. The polymeric products after different conditions and extents of reaction have been separated into uncombined rubber, two interpolymer fractions, and uncombined polymethyl methacrylate by fractional precipitation and extraction methods. The structure of the interpolymers has been investigated by measurement of composition and osmotic molecular weight, ozonolysis to degrade the rubber segments and isolation of the polymethyl methacrylate fragments, autoxidation of the rubber segments, and viscosity measurements on the uncombined rubber. The interpolymer is a linear block polymer containing one polymethyl methacrylate segment and of the order of one or two rubber segments per molecule. The Trommsdorff gel effect has a profound influence on the rate of formation, composition, and structure of the interpolymer.

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MASTICATION OF RUBBER. VI. VISCOSITY AND MOLECULAR WEIGHT RELATIONSHIPS FOR NATURAL RUBBER AFTER COLD MASTICATION *

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As with other polymers, many of the physical properties of natural rubber are dependent on the mean molecular weight of the rubber molecules, their chain length distribution, and extent of branching. Since the physical characteristics vary for natural rubber produced by different trees and are further altered during storage and the processing operation of mastication, it is interesting to find what correlations between properties exist, for example, between number average molecular weight and limiting viscosity number after different extents of mastication, and to consider how these correlations provide insight into the molecular changes taking place.

Comparisons of limiting viscosities and Huggins' constants[1], k' (of the viscosity number-concentration equation, $\eta/c = [\eta] + k' [\eta]^2 c$), have been made on rubbers masticated in air and in nitrogen and inferences drawn from increase in k' values of the occurrence of a branching reaction on mastication in air with certain radical acceptors and on mastication in nitrogen without added acceptors. Similarly, decrease in the Flory-Huggins' constant[2,3], μ (of the osmotic pressure-concentration equation, $\pi/c = RT(A + Bc)$, where $A = 1/M_2$ and $B = (\frac{1}{2} - \mu)/d_2^2 \bar{V}_1$ and d_2, M_2 are the density and molecular weight of the solute and $\bar{V}_1$ the molar volume of solvent), for rubber masticated in nitrogen again indicates a branching reaction. Increase in bulk viscosity of the rubber is another property shown to be dependent on branching.

The relationship obtained between limiting viscosity number and osmotic molecular weight on masticating in air provides a useful calibration of the latter against the easily measured former property. The exponent α' when the data are expressed by the usual Mark-Houwink equation, $[\eta]_u = K_u M_n^{\alpha'}$, has a value greater than unity, which value indicates that the parameter α' is not to be identified with the exponent α of magnitude 0.67 in the equation, $[\eta] = KM_n^{\alpha}$, of fractionated rubber[4] but is partly dependent on change in chain length distribution during mastication. The viscosity-osmotic pressure results for rubber samples masticated in nitrogen cannot be expressed by an equation of this type, but provide evidence of a branching reaction with relatively little change in number average molecular weight.

EXPERIMENTAL MATERIALS AND METHODS

Rubber.—Smoked sheet[5] was kindly supplied by the Rubber Research Institute, Malaya, and deproteinized crepe[6] by the J. P. P. Karet, Indonesia.

Smoked sheet was used only for determining the limiting viscosity number-molecular weight relationship on degradation in air (Figure 2).

Viscometry.—Ostwald viscometers of B. S. type 1[7] gave linear viscosity number-concentration curves in the range 0.1–0.5 g rubber in 100 ml benzene or other solvent at 20° C. Allowance was made for the kinetic energy of flow[7], which increased the uncorrected limiting viscosity numbers in benzene, carbon tetrachloride, hexane, and 15 per cent methanol-benzene by 4, 5, 8, and 4 per cent, respectively. The overall experimental limits of error in limiting viscosity numbers was ±3 per cent.

The Huggins' constant, k', was determined directly from the slope of the limiting viscosity-concentration curve since the overall experimental error of ±10 per cent in k' did not justify a more refined analysis[8]. The values of k' in benzene, carbon tetrachloride, n-hexane, and 15 per cent methanol-benzene would have been 8, 10, 16, and 8 per cent too high, respectively, if the kinetic energy correction had not been made[9].

Osmometry.—The osmometer was of Fuoss and Mead design[10] except for the substitution for needle valves of a mercury cut-off to isolate each half-cell from its filling tube and a glass siphon for draining[11]. One denitrated nitro-cellulose membrane was used throughout, possessing constant solvent permeability and less than 0.02 mm difference in levels with benzene in both half-cells after each molecular weight determination. A semidynamic equilibrium osmotic pressure value, π, was obtained by averaging readings over 2–3 hours in which equilibrium was almost attained from an initial 1 cm pressure difference. A static pressure value after 16–20 hours was also recorded to check for slow diffusion. Differences between static and semidynamic pressures were less than 5 per cent for the fractionated rubber samples and for the unfractionated samples of average molecular weight above 100,000. Molecular weights were calculated from the semidynamic equilibrium pressures.

Increasing slow diffusion was noted with unfractionated rubber of lower molecular weight. Average molecular weights of unfractionated rubber were thus increasingly overestimated with decrease in molecular weight, unfortunately by an unknown amount as it seems probable that the diffusion of relatively small molecules could not be inferred from the measured pressures.

As mentioned elsewhere[6], repeat osmotic pressure measurements were made at 25° C at two concentrations, approximately 0.3 and 1.0 g rubber in 100 g benzene, instead of the more usual single measurements at equidistant concentration intervals. Occasional measurements at 0.5 g/100 g confirmed the linear regression of π/c with c.

The semidynamic and static osmotic pressures gave equal slopes of π/c against c. Slow diffusion therefore did not cause a significant error in the determination of the interaction constant, μ. Taking the densities of rubber and benzene as 0.93 and 0.87 g ml^{-1}, the Flory-Huggins' equation is represented for convenience of calculation in the form, $\mu = 0.50 - 0.353 \times d(\pi c)/dc$. Limits of error in the measurement of slope increased from ±2 to ±12 per cent over the molecular weight range 100,000 to 1,000,000, giving an uncertainty to μ values of ±0.001 to ±0.004.

RESULTS

[η] and k' of masticated rubber.—Values of k' give a qualitative measure of branching. Higher values of k' have been found on preparing polymers in the presence of branching agents, for example, divinylbenzene in styrene, and the

inference made that higher values of k' by one process than by another denotes increased branching[12]. For natural rubber, the values of k' after masticating in nitrogen are consistently higher than after masticating in air (Figure 1), and have been interpreted[9] as due to a branching reaction consecutive to scission to
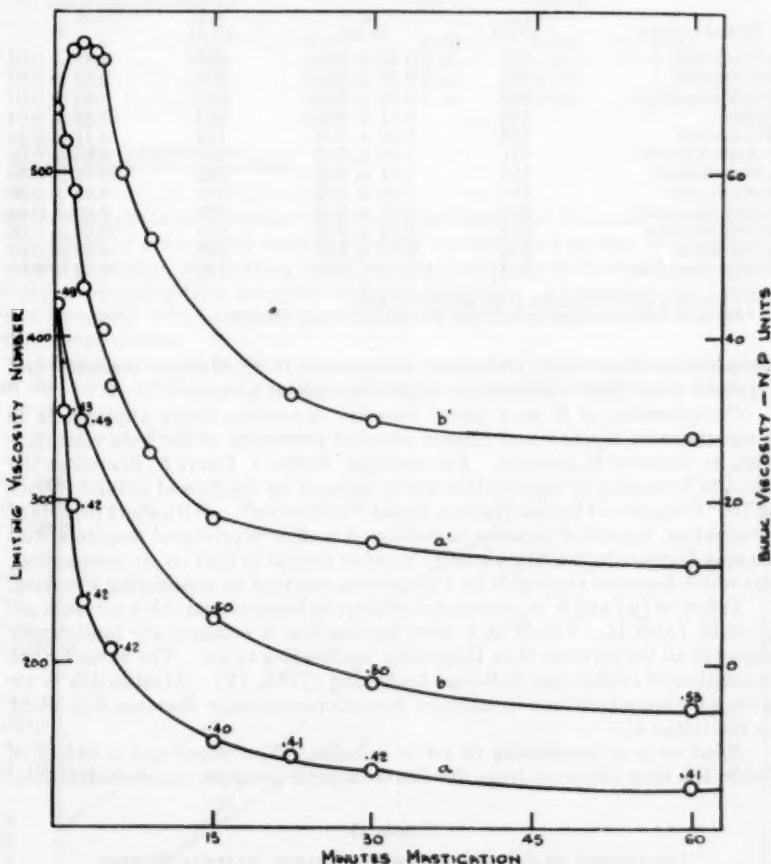
FIG. 1.—Limiting viscosity numbers and bulk viscosities (Wallace Plasticity Units) of natural rubber after mastication in air or nitrogen: a and b, $[\eta]$ on mastication in air and nitrogen, respectively; the numbers are the k' values. a' and b', bulk viscosities on mastication in air and nitrogen, respectively.

radicals by mechanical shear[12] occurring in nitrogen and mainly linear degradation occurring in air.

The results in Table I are further confirmation of this qualitative k' criterion for linearity of rubber molecules. These values of k' are a selection from the data providing the limiting viscosity numbers previously reported for rubbers masticated with different radical acceptors[13]. The Huggins' constants are in accord with the noncrosslinking and crosslinking reactivity of the radical

TABLE I

[η] AND k' FOR NATURAL RUBBER AFTER 30 MINUTES MASTICATION
IN AIR AND NITROGEN WITH RACIDAL ACCEPTORS
IN BENZENE AT 25° C

| | | | In nitrogen | |
Radical acceptor	$[\eta]$, g⁻¹ ml	k' (in air)	$[\eta]$, g⁻¹ ml	k'
α-Naphthol	210	0.39 ± 0.04	336	0.42 ± 0.04
Azobenzene	189	0.38 ± 0.04	306	0.43 ± 0.04
Naphthaquinone	202	0.35 ± 0.04	287	0.43 ± 0.04
Iodine	148	0.41 ± 0.04	233	0.45 ± 0.04
Thiophenol	162	0.42 ± 0.04	159	0.41 ± 0.04
p-Aminophenol[a]	541	0.72 ± 0.07	639	0.65 ± 0.06
n-Butyramide[a]	554	0.64 ± 0.06	582	0.64 ± 0.06
Benzoic acid[b]	183	0.38 ± 0.04	391	0.64 ± 0.06
Trinitrobenzene[a]	503	0.60 ± 0.04	301	0.63 ± 0.06
m-Nitroaniline[b]	218	0.37 ± 0.04	391	0.59 ± 0.06
p-Toluidine[b]	218	0.38 ± 0.04	385	0.63 ± 0.06
Maleic anhydride[b]	256	$0.38 + 0.04$	183	$0.59 + 0.06$

[a] Values of k' after masticating in air significantly high.
[b] Values of k' after masticating in air and nitrogen significantly different.

acceptors deduced from additional measurements of Mooney viscosity and expected from their reactivity in other free radical systems[12].

Consideration of k' as a useful viscosity parameter seems appropriate in comparisons of the flow and related physical properties of the bulk elastomer with its viscosity in solution. For example, Figure 1, Curve b', illustrates the effect of branching by mastication under nitrogen on the flow of natural rubber at 100° C measured by the Wallace Rapid Plastimeter[14]. With short periods of mastication, a marked increase in resistance to flow is produced despite a continuous decrease in limiting viscosity number similar to that on air mastication, but which becomes explicable by a branching reaction on considering k' values.

Values of [η] and k' of masticated rubbers in benzene and other solvents are given in Table II. Values of k' after masticating in nitrogen are consistently higher in all the solvents than those after masticating in air. The value for the unmasticated rubber also indicates branching (Table IV). Mastication in air gives a decrease in k' and in nitrogen a smaller increase or decrease dependent on the initial k'.

Effect on μ of masticating in air or nitrogen.—The slopes and μ values of Table III were obtained from the linear osmotic pressure/concentration-con-

TABLE II

COMPARISON OF [η] AND k' FOR MASTICATED NATURAL RUBBER
IN DIFFERENT SOLVENTS

Solvent		Mastication in air, min				Mastication in nigrogen, min			
		1	3	15	120	15	60	330	960
Benzene	$[\eta]$	304	175	136	89	250	165	110	106
	k'	0.41	0.39	0.41	0.43	0.52	0.51	0.55	0.52
CCl₄	$[\eta]$	340	209	174	111	320	218	145	135
	k'	0.51	0.43	0.46	0.44	0.59	0.58	0.60	0.61
n-Hexane	$[\eta]$	225	138	111	71	—	133	89	80
	k'	0.46	0.50	0.45	0.46	—	0.65	0.58	0.69
Benzene + 15% methanol	$[\eta]$	157	97	83	67	137	96	68	63
	k'	0.46	0.44	0.42	0.44	0.58	0.48	0.49	0.50

TABLE III

SLOPES OF π/c VS c CURVES AND μ VALUES OF NATURAL RUBBER AFTER
MASTICATION IN AIR AND NITROGEN

In air			In nitrogen		
Mol. wt. $\times 10^{-5}$	Slope of π/c-c	μ	Mol. wt. $\times 10^{-5}$	Slope of π/c-c	μ
4.95[a]	0.151	0.447	4.52[b]	0.206	0.427
1.96	0.190	0.433	3.95	0.197	0.431
1.36	0.216	0.424	2.64	0.179	0.437
1.02	0.235	0.417	1.36	0.164	0.442
0.77	0.227	0.420			

[a] Initial unmilled smoked sheet.
[b] Initial unmilled deproteinized crepe.

centration curves obtained for rubber samples masticated in air and in nitrogen.
The values of μ decreased from that of the unmasticated rubber to an almost
constant value on masticating in air, as would result from the increase in solu-
bility on changing from branched to linear molecules.   In contrast, the values
of μ increased with extent of mastication in nitrogen, again explicable by a
branching reaction.

*Limiting viscosity numbers and osmotic molecular weights after masticating
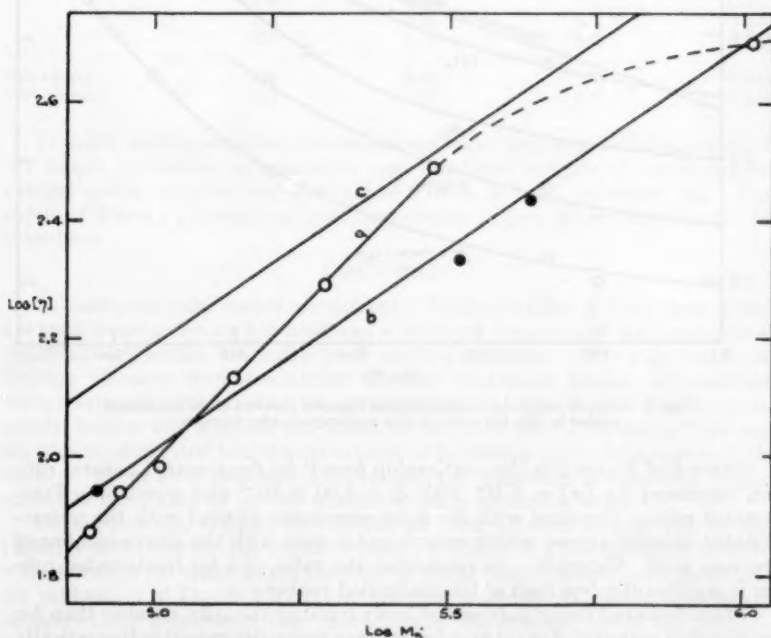in air.*—The intrinsic viscosities and osmotic molecular weights recorded in

FIG. 2.—Osmotic molecular weights-limiting viscosity numbers of unfractionated rubber after mastica-
tion in air: a and b, unfractionated masticated and fractionated rubber, respectively. c, theoretical curve
for a random distribution of chain lengths based on Curve b.

Figure 2, Curve a, can be related by an equation of the familiar Mark-Houwink type, $[\eta]_u = K_u M_n{}^{\alpha'}$ with $K_u = 5.55 \times 10^{-6}$ and $\alpha' = 1.05$. As will be discussed later, agreement with this expression is probably merely a consequence of the flexibility of the two parameter equation and the K_u and α' are not similar terms to those obtained with the unfractionated polymer[4]. It is noteworthy that the values of K_u and α' uphold some of the early investigations for which the Staudinger equation was applied[15]. Using the results of Table II, values of K_u and α' in carbon tetrachloride, n-hexane, and 15 per cent methanol-benzene are $K_u = 2.19 \times 10^{-5}$, 1.41×10^{-5}, and 3.55×10^{-5}, and $\alpha' = 0.95$, 0.95, and 0.85, respectively.
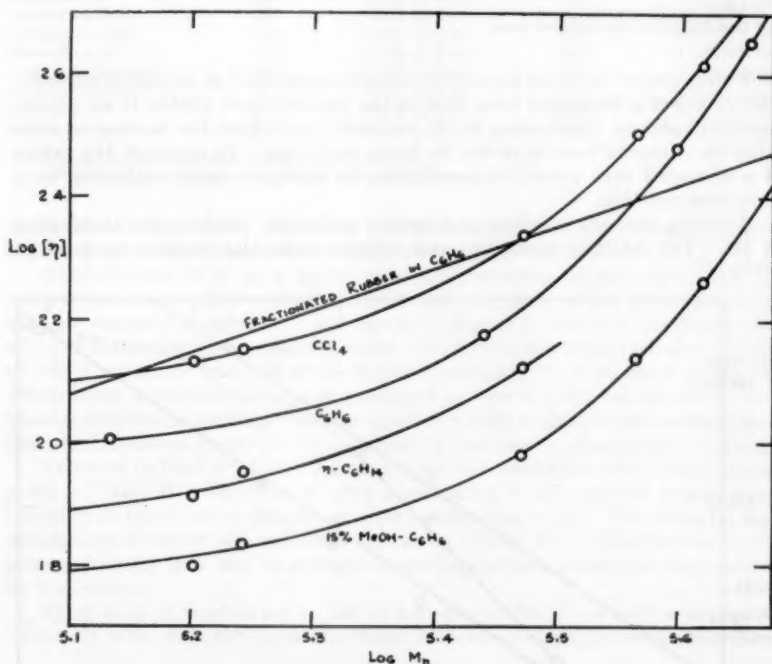

Fig. 3.—Osmotic molecular weights-limiting viscosity numbers of unfractionated rubber in different solvents after mastication under nitrogen.

Curve b of Figure 2 is the relationship found[4] for fractionated natural rubber, expressed by $[\eta] = KM^{\alpha}$ with $K = 5.00 \times 10^{-4}$ and $\alpha = 0.67$. Fractionated rubber measured with the same osmometer as used with the unfractionated samples agreed within experimental error with the above-mentioned previous work (Figure 2). In particular, the value of α for fractionated rubber is significantly less than α' for masticated rubber.

Unfractionated linear polymer of lower limiting viscosity number than for fractionated material of equal number average molecular weight is theoretically inexplicable, and therefore the molecular weights of heavily degraded masticated rubber appear to be experimentally overestimated (cf. "Experimental Meth-

ods"). The alternative explanation of a significant degree of branching is unlikely since the radical acceptor present, oxygen, is in sufficient concentration to make the scission reaction rate determining[13].

Limiting viscosity numbers and osmotic molecular weights after mastication in nitrogen.—Figure 3 presents the correlation between osmotic molecular weights and limiting viscosity numbers of deproteinized crepe in benzene solution after varying extents of mastication under nitrogen. The similar correlations with limiting viscosity numbers in other solvents are obtained from the data of Table II.

A large decrease in limiting viscosity numbers first occurs accompanied by a comparatively small change in overall average molecular weight, thus supporting the transfer and branching reaction previously put forward[9]. After only a moderate reduction in molecular weight, limiting viscosity numbers become markedly lower than those for fractionated rubber of equal number average molecular weight, again explicable by a branching reaction.

TABLE IV

VISCOSITY AND OSMOTIC MOLECULAR WEIGHT DATA[11] FOR NATURAL RUBBER LIGHTLY MASTICATED TO REDUCE GEL CONTENT BELOW 5%

Rubber	$[\eta]$, g^{-1} ml	k'	$M_n \times 10^{-5}$	μ
Smoked sheet	535	0.45	21.1	0.435
	406	0.58	7.1	0.435
	378	0.61	4.3	0.449
	358	0.39	6.5	0.435
Sole crepe	560	0.84	7.7	0.442
"F" rubber	605	0.57	6.2	0.448

Limiting viscosity numbers and osmotic molecular weights of unmilled rubber.— No simple correlation of viscosities and molecular weights of unmasticated natural rubber samples was obtainable[6] (Table IV) (cf. reference 16). The values of k' and μ substantiate the interpretation of lack of correlation as due to branching.

DISCUSSION

Viscosity-molecular weight correlations.—Natural rubber in fresh latex is not a wholly linear polymer but possesses a microgel component[16] and probably a significant proportion of soluble but branched molecules. The wide scatter of limiting viscosity numbers-number average molecular weights of unmilled rubber samples, in particular the great variability of molecular weight up to several million with intrinsic viscosities not normally above 700–800 g^{-1} ml, can likewise be attributed to different extents of branching of the molecules in bulk rubber. From an experimental viewpoint, the viscosities of unmilled rubber cannot be calibrated to provide number average molecular weights.

On mastication, samples of bulk rubber from different sources fall on the viscosity-molecular weight curve of Figure 2, Curve a, after moderate extents of degradation (to viscosities of the order of 300 g^{-1} ml). Empirically therefore, the calibration of Figure 2, Curve a, provides molecular weights of masticated natural rubber from viscosities. Structurally this appears due to the production of mainly linear chains of closely similar distribution in different rubber samples masticated to the same average molecular weight, but, as shown below, not according to the simple random degradation mechanism at first assumed[17].

Chain length distribution on masticating in air.—On the basis of an equal probability of rupture at any monomeric unit (random scission), it has been deduced[17] that changes in molecular weight distribution from an initial random distribution lead to viscosities of unfractionated randomly degraded polymers according to $[\eta]_u = K_u M_u{}^\alpha$, with $K_u = K\Gamma(\alpha + 2) = 1.509K$, where K and α are the constants obtained for the fractionated polymer. The theoretical curve[18] for randomly degraded natural rubber on the basis of the data for fractionated rubber is drawn in Figure 2, Curve c, and it is immediately obvious that the viscosity-molecular weight results for cold-masticated rubber are incompatible with the value of $\alpha = 0.67$ obtained on fractionation. Hence, chain rupture on cold mastication does not appear to occur randomly among the isoprenic units.

Instead, the empirical $\alpha' = 1.05$ means that monomeric units in long chains have a greater probability of rupture than those in short chains. A mechanism more in accord with the experimental results is that of Frenkel[19]. Frenkel has deduced that a polymer molecule of chain length greater than a critical value, x_0, becomes extended on being subjected to shear and eventually ruptured at a bond located in the central section between terminal chain segments of length $x_0/2$. Molecules less than x_0 are not ruptured under the given shear conditions.

The main experimental evidence for Frenkel's model is the limiting finite molecular weight attained on ultrasonic degradation of polymer molecules in solution. A similar limiting molecular weight appears to be the common experience in rubber mastication, and to have a value between 70,000–100,000 with a wide range of conventional milling and masticating machines. This limiting molecular weight is relatively insensitive to changes in temperature and rate of shear, and sets practical limitations on the extent of degradation of rubber by cold mastication. A limiting molecular weight of the above order also indicates that a significant proportion of the initial rubber chains escape degradation.

The derivation of molecular weight distribution functions on the basis of a model similar to Frenkel's is mathematically formidable and seems unwarranted until more critical data are available. However, many of the physical properties of unvulcanized rubber, the efficiency of vulcanization, and the aging of the vulcanizate depend on the molecular weight distribution, and so further experimental work appears worthwhile. It is readily seen that, qualitatively, mastication in air leads to a narrowing of the range of molecular weights until the major weight fraction possesses molecular weights in the region $x_0/2$ to x_0 and the homogeneity of molecular weight (as measured by the closer approach to unity of the ratio, weight average/number-average molecular weight) is increased. This is of significance in network formation, as by conventional vulcanization, and may account for other properties such as the experimental difficulty of fractional precipitation of masticated rubber.

SUMMARY

Values of limiting viscosity number, Huggins' interaction constant, k', osmostic molecular weight and Flory-Huggins' constant, μ, of masticated and unmasticated rubber have been compared. A calibration of limiting viscosity against molecular weight has been obtained for masticated rubber, but one is not available for unmasticated rubber due to the occurrence of different extents of branching. A mechanism is advanced of rupture during mastication of molecules above a critical molecular weight.

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OZONOLYTIC DEGRADATION OF INTERPOLYMERS OF NATURAL RUBBER WITH METHYL METHACRYLATE AND STYRENE *

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INTRODUCTION

The preparation of graft and block interpolymers of natural rubber and synthetic polymers[1,2] has made it desirable that the number and size of polymer chains attached to rubber be readily determinable. The degradation of unsaturated polymers with *tert*-butyl hydroperoxide in the presence of osmium tet oxide has been used for the determination of free polystyrene in SBR[3] and carbon black in several elastomers[4], and has recently been applied to the present problem[5].

The accurate determination of the rubber content of interpolymers by quantitative ozonolysis essentially according to the method of Boer and Kooyman[6] suggested that this might be made the basis of isolation of the attached polymer, the rubber being degraded into fragments of low molecular weight, from which the polymer could be separated by conventional techniques. The method should be applicable to any interpolymer, or mixture, of a polyunsaturated and a saturated polymer and is illustrated with reference to interpolymers of natural rubber (NR)-polymethyl methacrylate (PMM) and NR-polystyrene (PS).

EXPERIMENTAL

The sample of interpolymer, sufficient to yield *ca* 0.2 to 0.5 g free polymer after degradation, is dissolved in purified (alcohol-free) chloroform (50 ml) together with di-*n*-butyl sulfide (1.0 g). The NR content of the sample must be known either from analytical data or, preferably, by the quantitative ozonolysis of a second sample. Ozone (*ca* 0.3 mmole/min) is passed through the solution, maintained at $-25°$ in a reaction vessel of the type described by Boer and Kooyman[6], for 10 minutes longer than the theoretical time for complete reaction of the rubber. The solution is washed out into a 1 l beaker with chloroform (20 ml) and the PMM or PS precipitated with methanol (750 ml) containing calcium chloride (0.1%). The precipitate is collected, by centrifuging if necessary, washed with methanol (250 ml) and dried. Limiting viscosity numbers $[\eta]$ quoted in the results were measured at $25°$ using a B.S. No. 1 Ostwald viscometer over a concentration range 0.3–0.9 g per 100 ml benzene and are expressed throughout in units $(g/100 \ ml)^{-1}$.

DISCUSSION AND RESULTS

Chloroform is used as solvent because it combines good solubility characteristics toward the interpolymer, the free polymer and the degraded rubber with a reasonable ozone resistance.

TABLE I

CONTROL EXPERIMENTS USING HIGH MOLECULAR WEIGHT PMM
($[\eta] = 4.76$)

Wt. PMM, g	Wt. NR, g	Wt. sulfide, g	Ozonolysis time beyond theor. end point, min	PMM recovery, %	$[\eta]$ (recovered PMM)
0.5010	—	—	10	97	0.65
0.304	0.712	—	−5	—	4.6
0.307	—	1.0	10	97	3.7
0.306	0.701	1.0	10	96	3.6
0.530	0.509	1.0	5	—	4.0
0.417	0.503	1.0	20	—	2.8

PMM, as shown in Table I, and, to a lesser degree, PS are degraded in solution by ozone. While NR is present no free ozone is available in the solution to cause degradation of the polymer but in the time elapsing between recognition of the end point of the NR-ozone reaction and the removal of the free polymer from contact with ozone (*ca* 3–5 min) an appreciable fall in molecular weight may occur. The dialkyl sulfide prevents this, being of such intermediate reactivity[7] that the degradation of the NR proceeds unhindered, following which the sulfide reacts with ozone sufficiently rapidly to maintain the solution concentration of the latter at a very low level. The end point of the NR-ozone

TABLE II

CONTROL EXPERIMENTS USING LOW MOLECULAR WEIGHT PMM
($[\eta] = 0.605$)

Wt. PMM, g	Wt. sulfide, g	Ozonolysis time, min	PMM recovery, %	$[\eta]$ (recovered PMM)
0.520	1.0	5		0.57
0.520	1.0	10	88.1	0.57
0.520	1.0	15	88.5	0.56
0.520	1.0	20		0.52

reaction is not easily detectable under these conditions but ozonolysis may be safely continued some way beyond the calculated time.

Table I illustrates the protective action of the sulfide in control experiments using mixtures of NR and high molecular weight PMM in which degradation, followed by changes in limiting viscosity number, is easily detectable.

Table II shows that PMM of lower moecular weight is virtually completely protected from degradation and Table III confirms that no significant change in molecular weight distribution occurs under the specified conditions.

The results of the degradation of a NR/PMM block interpolymer are shown in Table IV, the independence of the limiting viscosity number of the isolated

TABLE III

OZONOLYSIS OF PMM FOR 10 MINUTES IN PRESENCE OF
DI-*n*-BUTYL SULFIDE (1.0 G)

Wt. PMM, g	Recovery, %	$[\eta]$		Osmotic mol. wt.	
		Original PMM	Recovered PMM	Original PMM	Recovered PMM
1.3567	98.9	1.22	1.20	223×10^3	223×10^3

PMM of time of overozonolysis indicating that degradation can be considered negligible.

Recovery of PMM is influenced by the fact that chloroform is an exceptionally good solvent for this polymer with the result that precipitation with methanol from chloroform solution is not completely quantitative. High recoveries (97–100%) are, however, obtained when the distribution of molecular weight of the polymer is such that the fraction having a molecular weight less than 30,000 is small. In the case of block interpolymers of NR/PMM prepared by cold mastication of NR and monomer[2], although $\bar{M}_n$ of the attached PMM is commonly of the order of 200,000, the distribution is wide and poly-

TABLE IV

DEGRADATION OF NR/PMM BLOCK INTERPOLYMER (35% PMM)

Wt. inter-polymer, g	Wt. sulfide, g	Ozonolysis time beyond theor., min	PMM recovery, %	$[\eta]$ (of recovered PMM)
1.492	0.0	0	85.5	0.59
1.492	1.0	5	87.5	1.06
1.492	1.0	10	86.9	1.08
1.492	1.0	15	85.4	1.12
1.492	1.0	20	85.5	1.06

mer recoveries of 85–90% are usual. Carrying out the ozonolysis in a mixed solvent (chloroform:carbon tetrachloride, 1:1) appears to have some advantage in this respect.

The method has also been applied to the degradation of interpolymers[2] of NR/PS. PS is not so susceptible to degradation by ozone as is PMM and also recoveries are generally higher than with the latter.

Since the degradation of the NR chains occurs via the double bonds, it follows that the liberated polymer chain will have as an end group any oxygenated fragment of NR of from 2 to 5 carbon atoms in length depending on the original structure of the interpolymer. Recovered PS and PMM are obtained

TABLE V

CONTROL EXPERIMENTS WITH PS ($[\eta] = 0.90$)

PS wt., g	Sulfide wt., g	Ozonolysis time, min	PS recovery, %	$[\eta]$ (of recovered PS)
0.400	1.0	5	97.5	0.83
0.391	1.0	10	97.0	0.94
0.391	1.0	15	97.0	0.92

pure within the limits of elemental or spectral analysis but the presence of the end groups appears to cause a decrease in the ease of flocculation of PS after precipitation and the polymer must usually be collected by centrifuging.

Further examples of the use of this degradative method will be found in the paper dealing with the detailed structure of interpolymers obtained by the cold mastication of NR and various monomers[3].

ACKNOWLEDGMENT

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SYNOPSIS

A simple ozonolytic method has been developed which enables the natural rubber trunk chains of rubber-polymethyl methacrylate and rubber-polystyrene interpolymers to be degraded into low molecular weight fragments from which the liberated polymer may be easily separated for characterization purposes. A dialkyl sulfide is used as a protective agent to prevent the attack of ozone on the polymer and the marked drop in molecular weight which would otherwise result.

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END GROUPS OF OXIDIZED RUBBER *

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Chain scission during the oxidation of polymeric 1,5-dimethyl-1,5-dienes occurs nearly quantitatively through the scission of an unusual peroxidic intermediate[1], followed ultimately by evolution of a group of fragments of low molecular weight at each scission[1-4]. The composition of this group depends on the reaction conditions. The first known stable intermediates to be formed subsequent to scission are levulinaldehyde and formaldehyde[4]:

$$
\begin{array}{cc}
CH_3 & CH_3 \\
| & | \\
RCH_2C=CHCH_2CH_2C=CHCH_2R' \rightarrow
\end{array}
$$

$$ (1) $$

$$ I \rightarrow (RCH_2\overset{\|}{\underset{O}{C}}CH_3) + $$

$$ CH_3\overset{\|}{\underset{O}{C}}CH_2CH_2CHO + CH_2O + $$

$$ (R'CO_2H) + H_2O \quad (2) $$
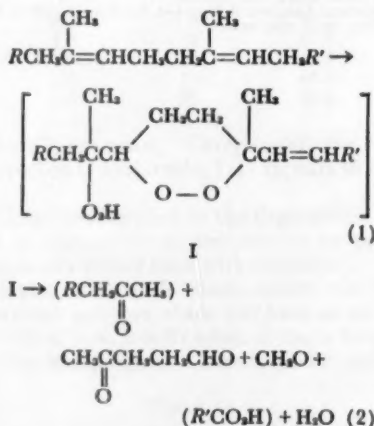
Bolland's kinetic[5] and analytic[6] studies combined with the requirements of the observed stoichiometry of scission form the basis on which it is possible to write a detailed mechanism[1] for the transformation represented by Equation 1. Nothing is known in detail of the sequence of reactions resulting in Equation 2. It has been suggested[7] that scission is associated with propagation rather than initiation—that is, with decomposition of a peroxy radical rather than of a hydroperoxide as is indicated in this scheme. This is still a moot point. It is now known, for example, that overall scission efficiency is strongly determined by temperature[1,3,8] and that benzothiazolethione[9] and o,o'-dibenzamidodiphenyldisulfide[10] both accelerate oxygen consumption as well as scission, in contrast to earlier belief.

Assignment of the end groups on the newly formed chain ends (in parentheses in the equations) in the original outline of this mechanism[1,2] was based on Naylor's[11] analyses of samples of a commercial oxidized rubber. It is assumed that the initial scission of a carbon-to-carbon bond occurs between the

two adjacent atoms each attached to oxygen, with the formation of a methyl ketone as one new chain end. This is followed by opening of the six-membered heterocycle and subsequent evolution of the two aldehydes. The chain end remaining has been presumed to go rapidly through the stages RCHO → RCO₂H. The high oxygen content of Naylor's samples indicates that they were oxidized at relatively low temperature[2,3], where over-all scission efficiency is low. Although "depolymerized" rubber of both low molecular weight and low oxygen content is available commercially, it seemed desirable to attempt to confirm directly the formation of the postulated end groups on samples oxidized under controlled conditions and not so severely "degraded".
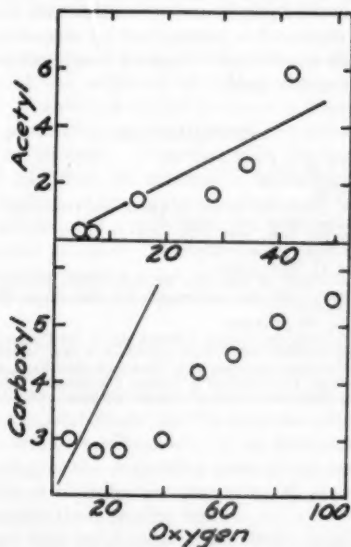
Fig. 1.—(Top) Methyl ketone. Fig. 2.—(Bottom) Carboxyl. Both are given as a function of oxygen consumed. Units are moles (equivalents) per 10⁵ g of rubber. Solid lines show the expected relations if one such end group is formed per scission.

The results[12] of estimates of acetyl and carboxyl end groups on a group of similar samples adjusted in molecular weight in the range 10^5 to 10^6 by oxidation at high temperature are presented in Figures 1 and 2.

Analyses were made on samples of a relatively pure rubber obtained from a commercial latex concentrated by creaming. The only further treatment consisted of leaching the samples with hot water (95° to 99° C) after they had been coagulated on forms. The samples were treated with oxygen at 140° C in an apparatus which has been described[4]. In this apparatus, the rubber is exposed to a flowing stream of gas so that volatile products are swept away. Under the conditions of this experiment, the measured scission efficiency (moles of chain cuts per mole of oxygen absorbed) is close to 0.1.

An unsuccessful effort was made to estimate total carbonyl content of the oxidized rubber by adaptation of a published method claimed to give high sensitivity and precision[13]. The iodoform reaction[14], which should be specific for

one end group, proved to be unexpectedly easy to use.   By making use of an observation by Fuson[15] the reaction was carried out on a solution of rubber in a mixture of chloroform and dioxane.   Rubber was precipitated by the addition of methanol, and iodoform was determined in the supernatant by comparison of the absorption at 347 mμ with a solvent blank.   In Figure 1 the results are plotted as methyl ketone end groups versus oxygen absorbed.   The solid line is that expected if one CH_3CO group is formed per scission.

Carboxyl groups were estimated by titration of 0.5- to 1.0-g samples of rubber with potassium methoxide in benzene solution, using phenolphthalein as indicator.   The results for one series of samples are plotted in Figure 2.

These results are in agreement with the hypothesis that the methyl ketone end groups are formed in the initial scission reaction and that the final structure of the other end group produced is determined by secondary reactions.   Under the conditions used in the experiments reported here, just under half the product is oxidized as far as carboxylic acid[16].

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ADHESION OF HIGH POLYMERS. 2. A METHOD FOR DETERMINATION OF THE MUTUAL ADHESION OF HIGH POLYMERS *

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The present communication deals with a problem of great practical importance—determination of the adhesion of a high molecular adhesive to a high molecular substrate. A solution of this problem is important for the footwear, rubber, paper, wood processing, and cardboard box industries, and in a number of other branches of technology. Together with the development of a method for determination of adhesion, we attempted to determine more precisely the influence of certain factors on the mutual adhesion of high polymers.

As is known the adhesion of a high polymer to a substrate can be characterized by: 1) the adhesion pressure, which is the minimum force required to detach the adhesive simultaneously over its total area of contact with the substrate, or 2) the work expended in a gradual stripping of the adhesive from the substrate.

In the development of a method for determination of mutual adhesion of high polymers, the second method of evaluation was chosen, for the following reasons: 1) we are mainly concerned with the strength of adhesion of thin films of high polymer to a hard substrate; in this case the adhesion strength is better characterized by the work of adhesion[1,2]; 2) in determinations of the work of adhesion exact centering of the detaching force is not needed, while this is necessary in determinations of adhesion pressure; 3) stripping tests give much more reproducible results than tearing tests[3].

The adhesive used was butadiene-acrylonitrile copolymer, containing 37.7 per cent acrylonitrile. The adhesion of this copolymer to the substrates used was not too high, so that the peeling apart of the joints was always adhesive in nature.

The substrates used were models of plant and animal fibers—thin, mirror-smooth films of regenerated cellulose (cellophane) and hardened and unhardened gelatin. It has been shown in a number of recent investigations that roughness of the substrate surface can have a great effect on adhesion[2,4,5].

Great importance was attached in this work to obtaining perfect contact between the adhesive and the substrate. A special technique was developed for producing a layer of adhesive from a solution of fairly low viscosity on the substrate surface for this purpose. The method used for determination of the work of adhesion did not differ in principle from the usual method of adhesion measurement by the pulling apart of a specially prepared joint with the aid of a recording dynamometer.

Preparation of joints.—The joints with cellulose substrate were made as follows: standard cellophane 30 μ thick was washed free of glycerin, stretched in

the wet state on some smooth, horizontal surface, and then dried in air. A closely fitting cardboard frame was placed on the dried cellophane film, and a definite quantity of 8 per cent solution of butadiene/acrylonitrile copolymer in pure benzene was then poured into it. After the solvent had partially evaporated, a layer of very fine cotton percale fabric was placed on the surface of the forming film. This fabric, which adhered to the outer surface of the adhesive layer, served as a reinforcement or base which prevented deformation of the adhesive layer when it was being peeled off the substrate. When the solvent had completely evaporated, the frame was removed and the joint was cut into strips of the required width. Complete contact between the adhesive and substrate was ensured by this method.

McLaren[6], who also used cellophane as substrate, used a somewhat different technique. To obtain the joints he coated technical cellophane (not washed to remove glycerin) with adhesive solution, allowing the solvent to evaporate from the film surface, and then joined two layers of film under pressure at a temperature 30° above the softening point of the adhesive. This method has a number of serious faults, one of which is the presence of glycerin, which undoubtedly affects adhesion, in the cellophane; the possibility of incomplete coalescence of the polymeric adhesive layers during the relatively short contact time; the effect of heat on the properties of the substrate and adhesive, etc.

The preparation of joints with a gelatin substrate was much more complicated. In this case solutions of both components had to be used. Prolonged experimental work showed that the following procedure was the most suitable for the preparation of such joints. A cardboard frame was placed on a mirror-smooth surface of a polyvinyl chloride film (PVC lacquer), and 2 per cent aqueous solution of edible gelatin (All-Union Standard 98) was poured into the frame in sufficient quantity to form a film about $50\,\mu$ thick. This thickness gave a gelatin film of adequate strength and high elasticity.

When the gelatin film was completely dry, 8 per cent solution of butadiene/acrylonitrile copolymer in benzene was poured over it. After some time, when the benzene had partly evaporated, a layer of fabric (percale) was carefully placed on the forming layer of adhesive. After final drying and removal of the joint from the support it was cut into strips of the required width.

When hardened gelatin films were used, a solution of basic chromium salts with a basicity of 41.5 per cent to give 1 g of Cr_2O_3 per 100 g of air-dry gelatin, was added to the gelatin solution before it was poured into the frame.

EXPERIMENTAL

The joints were peeled apart in a dynamometer, the jaws of which moved horizontally. Thus the stripping was effected at an angle of 180°. The dynamometer was equipped with reducing gear to make it possible to separate joints at different speeds. A diagram for the stripping force as a function of specimen length could be obtained by means of the recording device.

The specific work of adhesion Ad was calculated from the equation:

$$Ad = \frac{P2lg}{lb} = \frac{2Pg}{b},$$

where P is the average force of separation, found from data for a number of points 1 cm apart on the adhesion diagram; l is the length of the effective part of the joint; b is the width of the joint; g is the acceleration due to gravity.

Since the substrate film and the fabric-reinforced adhesive film were both thin and very flexible, and did not undergo irreversible deformations during the separation, no corrections were applied for the work of deformation of the films. The nature of the contacting surfaces of adhesive and substrate were always examined after separation.

It was assumed that the values obtained characterized adhesion only if both surfaces were mirror-smooth. When the substrate surface after separation was covered with a thin film of adhesive, while the adhesive surface was dull and uneven, it was assumed that the separation took place in the adhesive and that forces of cohesion had been overcome. In many cases mixed separation occurred—in some parts of the joint the separation was adhesive and in others, cohesive. All the values for adhesion given below are average results for 8–10 parallel determinations.

Effect of separation rate on the work of adhesion.—It is reported in a number of publications[1,2,4,7-9] that the nature of the separation and the work of adhesion depend on the speed with which the adhesive film is separated from the substrate.

It was important to determine the influence of the separation rate on adhesion in the conditions of our experiments. Joints of chrome-tanned gelatin

TABLE I

EFFECT OF THE SPEED ON THE SPECIFIC RESISTANCE TO SEPARATION
AND THE SPECIFIC WORK OF ADHESION

| v in cm/sec | Type of separation, and P in g/cm | | | Ad in ergs/cm² |
	Adhesive	Mixed	Cohesive	
0.083	—	381	451	—
0.166	74.3	237	—	145,780
0.250	78.6	—	—	154,210
0.300	76.3	—	—	149,700

and butadiene/acrylonitrile copolymer were separated for this purpose at speeds from 0.083 to 0.3 cm/second. The gelatin film thickness in these experiments was 47μ (or 0.0058 g gelatin per 1 cm²), and the thickness of the adhesive film was 218μ (0.0215 g/cm²). The width of the joint was 4 cm, and its effective length 10 cm. The results of the experiments are shown in Table I.

Table I shows that, in full agreement with literature data[1,2], mixed and cohesive types of separation occur only at low speeds, of the order of 0.083–0.166 cm/second. At higher speeds the separation was purely adhesive in character. The reason is that during slow separation, when the deformation rate is less than the relaxation rate, the adhesive behaves as a liquid. In consequence the joint is broken when the cohesive forces of the adhesive are overcome. At high separation speeds, however, the adhesive behaves as a solid with a high modulus of elasticity and the separation occurs along the interface. No increase was found in the value of the work of adhesion with increasing separation rate in our experiments.

An interesting feature is that in the case of purely cohesive separation at low speeds the separation curve is of zigzag form. This is seen in Figure 1, which shows adhesion diagrams typical of cohesive, mixed, and purely adhesive separation (the ordinate axes show the distance from the start of the working part of the joint, and the abscissa axes give the corresponding separation force). Figure 1 also shows that in the adhesion diagram for the mixed type of separa-

tion the maximum values of the resistance to separation correspond to cohesive separation.   These peaks alternate with regions of purely adhesive separation, parallel to the ordinate axis.

The transition from adhesive separation to the cohesive form, less advantageous from the energy standpoint, is probably explained by weak spots on the adhesive surface and by the fact that after a tear is formed the stress is concentrated in its lower part.   As a result, further separation proceeds not along
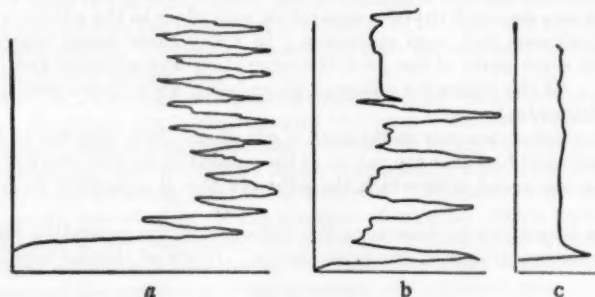

Fig. 1.—Typical separation resistance—joint length curves: a) for cohesive separation (at low speeds); b) for mixed separation (at medium speeds); c) for adhesive separation (at high speeds).

the interface (where the resistance to separation is less) but along the adhesive layer.   This separation will continue until for one reason or another the tear reaches the adhesive-substrate interface.   This is clearly seen in the scheme in Figure 2.   It is still not clear why, with purely cohesive separation, there is a distinct periodicity in the fluctuations of the separation force.   As the speed increases, the periodicity of the adhesive separation also begins to increase and at sufficiently high speeds a curve corresponding to purely adhesive separation
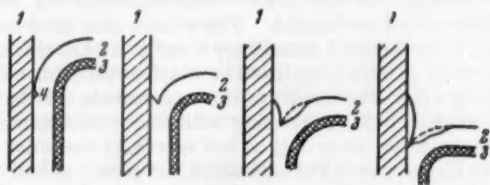
Fig. 2.—Scheme for the transition from adhesive to cohesive types of separation, and back: 1) substrate; 2) adhesive; 3) reinforcing fabric; 4) fault on the surface of the adhesive layer.

is obtained.   Since a speed of 0.3 cm/second always ensured adhesive separation in our conditions, all the subsequent experiments were performed at this speed.

Effect of the width of the joint on adhesion.—As we found in one of our investigations that in determinations of autohesion the results may be influenced by the contact area[10], experiments were carried out to determine the effect of joint width on the specific work of adhesion.

The substrate in these experiments was a film of chrome-tanned gelatin $\sim 50 \mu$ thick.   The layer of adhesive, butadiene/acrylonitrile copolymer, was $\sim 250 \mu$ thick. The length of the working part of the joints was 10 cm in all

cases, and the width was varied between 1 and 5 cm. The separation of the joints was carried out at the same speed of 0.3 cm/second. The results of the experiments are shown in Table II.

The results in Table II show that the specific work of adhesion does not depend on the width of the specimen. In the subsequent experiments joints 2 cm wide were used in all tests; the length of the working part of the joint was always 10 cm.

Effect of thickness of the adhesive layer on adhesion.—It has been shown by McBain[11] and a number of others[12-18] that the adhesive strength always in-

TABLE II

EFFECT OF JOINT WIDTH ON THE SPECIFIC RESISTANCE TO SEPARATION AND THE SPECIFIC WORK OF ADHESION

Width of specimen, cm	P in g/cm			Ad in ergs/cm²
	Minimum	Maximum	Average	
1	115.0	120.0	118.7	232,800
2	99.0	117.0	108.2	212,300
3	109.6	126.0	116.0	227,600
4	108.8	118.8	111.8	219,300
5	104.0	124.0	111.2	218,100

creases with decreasing thickness of the adhesive layer. Several theories have been advanced to explain this effect[13-15].

However, they all explain the increased adhesive strength with decreasing thickness of the adhesive layer in terms of the properties of the adhesive substance itself. In addition, most of these theories are only applicable when the joint is broken along the layer of adhesive. In this situation, in an investigation the aim of which was to develop a method for the evaluation of the adhesive power of high polymers, it was necessary to determine the influence of layer thickness on adhesion proper, determined by the peeling method.

TABLE III

EFFECT OF THE THICKNESS OF THE LAYER OF ADHESIVE ON THE RESISTANCE TO SEPARATION AND SPECIFIC WORK OF ADHESION

Thickness of adhesive layer, μ	P in g/cm	Ad in ergs/cm²
152	100	196,200
253	135.5	265,850
354	113	221,600
456	105	206,000
557	113	221,600

Experiments for this purpose were carried out with joints in which chrome-tanned gelatin was used as substrate. The preparation and separation of the joints was carried out according to the standard procedure, except that the thickness of the layer of adhesive was varied between 152 and 557 μ, corresponding to 0.015 to 0.055 g of adhesive per 1 cm² of substrate. The results are shown in Table III.

Table III shows that the specific work of adhesion is practically independent of the thickness of the adhesive layer. This is possibly explained by the fact that the layers of adhesive used in our experiments were not thin enough.

There are indications in the literature that in certain cases the adhesive strength increases appreciably only with very thin layers of adhesive[16]. In our view, however, another explanation is more probable, namely that adhesion proper is independent of the thickness of the layer of high molecular adhesive.

All the subsequent experiments were carried out with an adhesive layer thickness of 253 μ, which corresponds to 0.025 g of adhesive per 1 cm^2 of substrate.

Effect of the pressure applied to the joint on the work of adhesion.—When two unlike solid surfaces are brought into contact, the force of adhesion, as a rule, depends on the contact pressure. The usual explanation for this is that increase of pressure increases the area of true contact by changing the shape of the surface.

It was desired to determine the effect of pressure on the work of adhesion in our conditions, when the adhesive was applied to the substrate in solution form. Experiments were therefore carried out in which joints made by the usual method were subjected to various pressures for 40 minutes and immediately separated. Cellophane was used as the substrate.

TABLE IV

EFFECT OF HEAT TREATMENT OF THE JOINT ON THE SPECIFIC RESISTANCE TO SEPARATION AND SPECIFIC WORK OF ADHESION

Heating temperature, ° C	P in g/cm			Ad in ergs/cm	Type of separation
	Minimum	Maximum	Average		
Without heating	115	121	117	229,550	Adhesive
25	119	134	126	247,210	Adhesive
50	128	154	146	286,450	Adhesive
75	118	400	183	359,040	Mixed
100	160	455	250	490,500	Mixed

The experiments showed that the work of adhesion is not changed by increase of pressure on the joint, but practically retains its initial value. Probably application of the adhesive to the substrate surface in solution form ensures complete contact between the surfaces of the two polymers, and further increase of contact area by the action of additional pressure cannot occur in this case.

Effect of heat treatment of the joint on the work of adhesion.—Voyutskiĭ and Zamaziĭ[17] showed that heat treatment of the joint has a very strong effect on autohesion of high polymers. We therefore studied the effect of heating the joint on the adhesion of a high molecular adhesive to a high molecular substrate.

Cellophane was used as the substrate in these experiments. The joints were prepared as described above, with the exception that the film of adhesive was formed by evaporation of the solvent in a cold room at a temperature close to zero.

The joints were heated for 40 minutes at 25, 50, 75, and 100° under a pressure of 100 g/cm^2, cooled, and held to constant weight in the cold in an atmosphere with 30 per cent relative humidity before separation. Joints obtained at 0° and not heated were also tested. The results are shown in Table IV.

It is seen from Table IV that heating of the joint sharply increases the work of adhesion. After heating to 75 and 100°, the adhesion increases so much that separation of the joint assumes a mixed character. In some regions of the

joint the separation proceeds along the interface, and at others in the adhesive, leading to a sharp increase of the difference between the maximum and minimum values of the resistance to separation. This indicates that in such cases the magnitude of the adhesion is close to the cohesive strength of the adhesive.

The increase of adhesion as the result of heating of the joint cannot be explained here by an increase of the true area of contact between adhesive and substrate, since when the adhesive is used in solution form this area is at its maximum and is close to the area of nominal contact. In our opinion the positive influence of heat on adhesion between two high polymers is due to the same causes as the influence of heat on autohesion. Thermal motion is increased as the result of increased temperature and molecules of the adhesive, or separate regions of them, diffuse into the substrate. It is possible that at sufficiently high temperatures partial diffusion of the substrate molecules into the adhesive may also occur. Both these processes lead to disappearance of a sharp boundary between adhesive and substrate, to formation of a firm weld between the two high polymers, and therefore to an increase in the strength of the adhesive joint.

TABLE V

EFFECT OF THE TIME OF CONTACT BETWEEN ADHESIVE AND SUBSTRATE
ON THE SPECIFIC RESISTANCE TO SEPARATION AND SPECIFIC
WORK OF ADHESION

| Contact time, days | P in g/cm | | | | P in g/cm | | | |
	Minimum	Maximum	Average	Ad in ergs/cm	Minimum	Maximum	Average	Ad in ergs/cm
					Joints with tanned gelatin substrate			
	Joints with cellophane substrate							
7	100	115	107	209,930	61	71	68	133,410
15	120	154	138	270,750	78	88	83	162,850
31	150	150	150	294,300	106	112	109	213,860
60	155	188	170	333,540	120	148	125	245,250
90	178	189	185	362,970	165	193	180	353,160
120	163	190	173	339,420	177	238	217	425,750

Quite obviously, mutual diffusion of molecules from two layers of high polymers brought into contact can occur only if these polymers are mutually soluble. Therefore the increase of adhesion as the result of heat treatment of the joint can also be regarded as the result of increased mutual solubility of the polymers on heating (see Reference 19).

Another explanation of the increased adhesion as the result of heating the joint may be based on the fact that heating leads to a more rapid redistribution of intermolecular bonds and facilitates orientation of molecules of the adhesive, or separate regions of them, at the substrate surface. The molecules of the adhesive can be regarded as joined together at their polar groups. This, of course, will hinder their orientation at the substrate surface, which is necessary for the formation of a firm adhesive joint. As the result of increased thermal motion on heating, these bonds are broken and the polar regions are more easily orientated at the substrate surface, forming bonds with the polar groups at that surface. This will naturally result in increased adhesion.

However, this theory, advanced by McLaren and his associates[6,18], hardly seems valid in the present instance, as the adhesive layer was formed from solution, in conditions when orientation of the molecules of adhesive at the substrate surface is not hindered in any way.

Effect of the time of contact between adhesive and substrate on the work of adhesion.—In studies of the influence of various factors on adhesion it was noticed that the force of adhesion of a high molecular adhesive to a high molecular substrate varies with time.   This fact is undoubtedly important, as it indicates, in the same way as the influence of temperature on the strength of the adhesive joint, a similarity between adhesion and autohesion.

Special experiments were carried out on the influence of the contact time on the work of adhesion, cellophane and chrome-tanned gelatin being used as substrates.   Before separation, the joints were kept for various times in an atmosphere at 30 per cent relative humidity when the substrate was cellophane, and at 60 per cent relative humidity when the substrate was gelatin.

The results of these experiments are shown in Table V.

Table V shows that the work of adhesion increases with increasing contact time.   This, like the increase of adhesion as the result of heat treatment, may be explained by diffusion of the adhesive into the substrate and of the substrate into the adhesive.   However, the work of adhesion does not reach the values attained when the joints are heated even after very long contact times.   Moreover, the values of the adhesion tend to a definite limit with increasing contact time, while no such limit is found with the use of heat.   This may be explained on the grounds that increase of temperature not only favors accelerated diffusion, but raises the mutual solubility of the polymers.

SUMMARY

1. A simple and fairly accurate method for determination of adhesion between two high polymers has been developed, based on separation of the joints by a peeling method.

2. It was found, in agreement with data available in the literature, that the manner of separation of the joints changes with variations of the speed of separation.   At low speeds, separation of polymer-polymer joints is cohesive in character, at moderate speeds it is mixed, and at high speeds it is purely adhesive.   No increase of the work of adhesion with increasing speed of separation was found.

3. It is shown that the width of the joint does not affect the results of the adhesion determinations.

4. It was found that in the limits studied (from 150 to 550μ) the thickness of the polymeric adhesive layer does not affect the value of the specific work of adhesion.

5. It is shown that if the layer of high molecular adhesive on the substrate is formed from solution, the pressure to which the joint is subjected after it is made does not affect the adhesion.

6. It was found that heat treatment of the joints considerably increases adhesion.

7. It is shown that adhesion increases and tends to a definite limit with increasing time of contact between a high molecular adhesive and a high molecular substrate.

8. It is suggested that the increase of adhesion by heat treatment and by increased contact time is caused by diffusion of molecules of the adhesive into the substrate and vice versa, which leads to disappearance of the interphase boundary and to formation of a stronger adhesive joint.

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CROSSLINKING OF ORIENTED RUBBER *

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INTRODUCTION

When rubber is subjected to the effect of high energy radiation, crosslinking occurs even in the absence of the usual vulcanizing agents. This effect parallels the crosslinking of other long-chain polymers by radiation and does not primarily depend on the presence of unsaturated bonds.

Crosslinking by radiation has the advantage that the process can take place over a range of temperatures which are not determined by the temperature needed to initiate the chemical changes involved in vulcanization. It should therefore be possible to obtain rubber with different elastic properties in different directions by irradiating oriented rubber at a temperature at which rearrangement of the molecules cannot take place. The efficiency of the process may be expected to show some small temperature-dependence in line with results obtained for radiation induced degradation of polymethyl methacrylate and polyisobutylene and the crosslinking of polyethylene. A small temperature variation is also found in the production of unsaturation in the main chain of polyethylene.

In unoriented material, the degree of crosslinking of an elastic network can be deduced from the relationship between the applied stress f and the strain. The formula may be written in the form:

$$f = \rho R T M_e^{-1} \left(\alpha - \frac{1}{\alpha^2} \right)$$

where ρ is the density of the polymer, R is the gas constant, T is the absolute temperature, and α is the ratio of the elongated length l divided by its original value l_0. When end effects may be neglected, the average molecular weight between crosslinks M_c is inversely proportional to the density of crosslinks, which is itself proportional to the radiation dose, i.e., to the total amount of high energy radiation absorbed. This has been shown in previous published work using both swelling in decane and elastic modulus for low elongations as methods of measuring M_c. This earlier work was confined to atomic pile radiation but present results indicate similar results when electron radiation is used.

EXPERIMENTAL

Degree of orientation.—Initial attempts to produce crosslinking in a specimen of completely uncured smoked sheet stretched during the irradiation process proved impossible due to plastic flow and uneven stretching. To reduce this plastic flow, very light radiation doses were given to the uncured specimen and this was then reirradiated in a stretched condition. However, no permanent marked orientation was observed, possibly due to the very small initial

dose used, which was unable to prevent cold flow during the subsequent highly stressed condition. These preliminary doses could not be greatly increased without in themselves counteracting the effect of further radiation on a subsequently stretched material. To overcome these difficulties, smoked sheet specimens were used which had previously been oriented during the calendering process. The smoked sheet was stretched during removal from the calender while being cooled below the flow temperature and immediately clamped between wax paper sheets. In this way, a permanently oriented material was obtained. The amount of residual stress was determined by heating 2 inch square pieces, 0.125 inch thick to 90° C for 10 minutes and then measuring
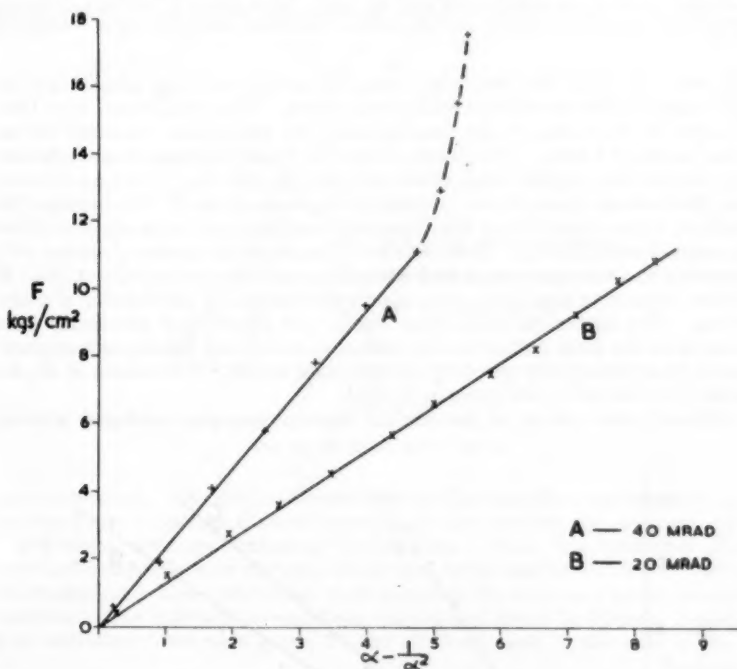
Fig. 1.—Annealed rubber.

their new dimensions. These showed a decrease in length in one direction of 40 per cent and an increase at right angles of 44 per cent; the thickness increase was about 15 per cent. The degree of inherent strain as compared with the annealed sample was therefore 67 per cent.

Annealed sheet.—Sheets of the annealed material were subjected to high energy radiation in the form of 2 Mev electrons from a Van de Graaff machine. The doses were given in a series of exposures during each of which one megarad of radiation dose was accumulated. This dose, if completely used in increasing the temperature of the specimen, would raise this temperature by 5°. Intervals were therefore allowed between exposures for the specimen to cool. The total accumulated doses were 20 and 40 megarad (Mrad). Dumb-

TABLE I

Radiation dose, Mrad	Treatment	Direction	$M_c{}^a$	% of units cross- linked	ev/ cross- linked unit	G^a
40	Oriented	Parallel	8.3×10^3	0.82	34.5	1.45
	Oriented	Perpendicular	13.0×10^3	0.52	54.0	0.92
	Oriented	45°	10.0×10^3	0.68	41.5	1.20
20	Oriented	Parallel	9.3×10^3	0.73	19.3	2.60
	Oriented	Perpendicular	20×10^3	0.34	41.5	1.20
	Oriented	45°	16×10^3	0.43	33.3	1.50
40	Annealed		11.5×10^3	0.59	47.7	1.05
20	Annealed		21×10^3	0.32	43.6	1.16

[a] The M_c and G values for oriented rubber, being deduced from the theoretical equation for an unoriented system, should be considered purely as useful parameters. The G values are the number of crosslinks per 100 ev.

bells were cut from the irradiated annealed specimens, both parallel and at right angles to the direction of initial orientation. These specimens were then subjected to increasing static loadings and the extensions measured for an initial length of 1 inch. The results plotted in Figure 1 show a linear relationship between the applied static stress and the quantity $(\alpha - 1/\alpha^2)$ as required from the formula given above. At high elongations of the 40 Mrad sample the observed values depart from this linear relationship, as is to be expected from the onset of crystallinity. There was no difference in the strains observed with increasing and with decreasing load during the complete cycle of about 20 to 30 minutes indicating that little or no plastic flow occurs at this density of crosslinking. The higher radiation dose chosen (40 Mrad) had previously been found to be the most useful dose for radiation curing and corresponds approximately to a rubber fully cured by conventional means. The values of M_c deduced from this curve are given in Table I.

Oriented sheet.—Some of the original material was also irradiated without
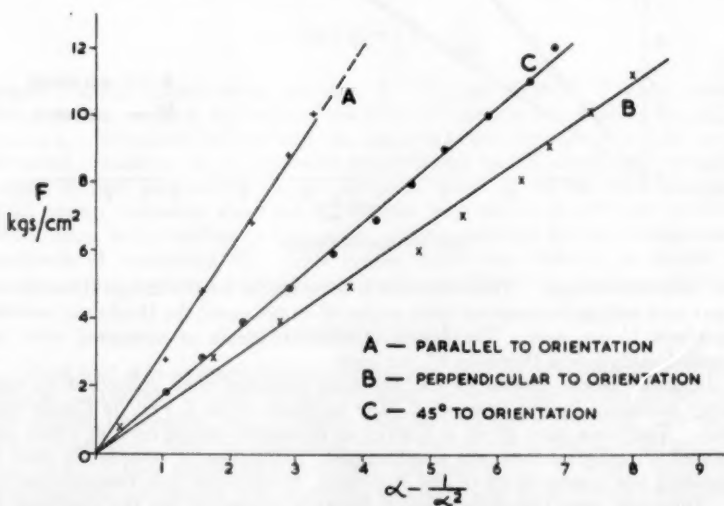
FIG. 2.—20 Mrad oriented rubber.
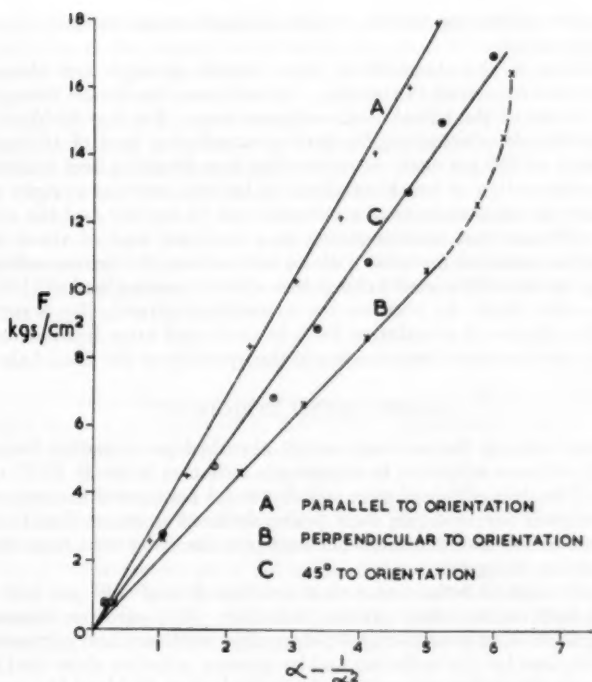
Fig. 3.—40 Mrad oriented rubber.

prior annealing. The total radiation time for the same dose was extended over several hours to ensure that no appreciable temperature rise occurred which might allow some reorientation or annealing. From the irradiated sheet, standard dumbbells were cut parallel, at right angles and at 45° to the direction of orientation. These dumbbells were tested in the same way as the annealed material. The relevant stress/strain curves are given in Figures 2 and 3. Two radiation doses were given, 20 and 40 Mrad, and, in the case of the 40

TABLE II

Radiation dose, Mrad	Treatment	Direction of stretching w.r.t. orientation	Tensile strength calc. on initial cross-section kg/cm²	Elongation at break, %	Tensile strength calc. on cross-section at break, kg/cm²
40	Oriented	Parallel	130	900	1300
	Oriented	Perpendicular	125	900	1250
	Oriented	45°	128	900	1280
20	Oriented	Parallel	10	250	35
	Oriented	Perpendicular	75	1300	1050
	Oriented	45°	55	1000	600
40	Annealed		153	875	1490
20	Annealed		80	1300	1120

Mrad sample, points are shown at high elongations to indicate the onset of crystallinity values.

In addition to the stress/strain data, tensile strength and elongation at break were also measured (Table II). In each case the tensile strength is calculated in terms of the initial cross-sectional area. For the 20 Mrad sample, in the direction of orientation, fracture occurred at a load of 10 kg/cm^2 and an elongation of 250 per cent, corresponding to a breaking load (calculated on the final cross-section at break) of about 35 kg/cm^2, whereas at right angles to the direction of orientation tensile strength was 75 kg/cm^2 and the elongation at break 1300 per cent, corresponding to a breaking load of about 1050 kg/cm^2. For the annealed material with no orientation, the corresponding figures were 80 kg/cm^2 at 1300 per cent elongation with a breaking load of 1120 kg/cm^2. Attempts were made to observe the orientation directly by x-ray diffraction but the degree of orientation both initially and after irradiation was insufficient to produce any dissymmetry in the intensity of the usual halo pattern.

CROSSLINKING EFFICIENCY

Previous data on the average energy absorbed per crosslink formed were given for specimens subjected to atomic pile radiation in the B. E. P. O. pile at Harwell. The data obtained were as follows: 1.1 per cent of the isoprene units were crosslinked per unit pile dose (value deduced from swelling in decane); 0.7 per cent of the isoprene units per unit pile dose (deduced from the elastic modulus at low elongation).

Unit pile dose is defined as a slow neutron flux of 10^{17} per cm^2 plus the associated fast neutron and gamma radiation. Comparative measurements on the degradation or crosslinking of polymethyl methacrylate, polyisobutylene, and polyethylene by pile radiation and by gamma radiation show that for these materials one pile unit is approximately equivalent to 45 Mrad of gamma radiation. It is usual to give radiation induced reactions in terms of a G value, which is defined as the number of chemical changes of a given type produced per energy absorption of 100 ev. By definition, a radiation dose of one megarad corresponds to an energy absorption per gram of 0.625×10^{20} ev per gram so that, using the above equivalent, one pile unit would correspond to a total energy absorption of about 28×10^{20} ev per gram.

Per 100 isoprene units of total molecular weight 6800, the energy absorbed corresponding to one pile unit would be $6800 \times 1.66 \times 10^{-24} \times 28 \times 10^{20}$ or 31.8 ev. Since there are two crosslinked isoprene units for every crosslink, the G value for crosslinking by pile radiation is 1.7 (decane swelling measurements) and 1.1 (elastic modulus measurements).

In the present experiments, the value of M_c deduced from the annealed samples was 1.15×10^4 (169 isoprene units) for an electron radiation dose of 40 Mrad. For this high radiation dose, end effects are relatively unimportant; the number of chains between crosslinks is equal to the number of crosslinked units and is twice the number of crosslinks. The energy absorbed per chain of molecular weight M_c is $40 \times 0.625 \times 10^{20} \times 1.15 \times 10^4 \times 1.66 \times 10^{-24}$ or 47.7 ev. The energy absorbed per crosslink is therefore 95.4 ev and the G value per crosslink is 1.05 in good agreement with the previous value based on the elastic modulus. This agreement is perhaps better than might be expected in terms of the accuracy of dosimetry and of the different methods of measuring crosslinking. It does, however, indicate that the effect of pile radiation is similar to that of electron radiation, depending only on the energy absorbed and

not on the type of radiation (fast neutrons and gamma radiation in the pile, electron radiation in the present work) nor does it depend on the rate of delivery which was about 3 Mrad per hour in the atomic pile as against intermittent pulses each of 1 Mrad per second in the electron beam.

For the oriented specimens, the above theoretical formula does not apply but it can nevertheless be used to give an "equivalent" value of M_c. The values deduced using this formula are given in Table I. From them, the G values for "equivalent" crosslinking are deduced.

The G values for the lower radiation doses are less reliable than for the 40 Mrad specimens owing to the increased importance in the former case of end effects due to the finite initial molecular size. The values obtained for the 40 Mrad oriented sample straddle the value obtained for the unoriented material subjected to the same radiation dose.

DISCUSSION

The linear relationship observed between the applied stress and the elongation function $(\alpha - 1/\alpha^2)$ is found to hold over a considerable range of extensions up to the point at which crystallinity intervenes. This is a direct confirmation of the network theory of elasticity.

The molecular orientation present in the original rubber used in these tests arises from the entanglement of molecules (and possibly partial crystallinity) introduced during the fabrication process. It is not due to a small amount of crosslinking or vulcanization since the initial material is readily soluble; moreover, when the specimen is heated to allow molecules to become free of their entanglements and crystalline regions, these molecules move to positions of greater entropy, the specimen changes dimensions and loses its anisotropic character.

In irradiated oriented rubbers, this is not the case and the orientation acquired is permanent in character. During irradiation, no significant change in dimensions is observed, nor does any such change occur when an irradiated sample is heated for 20 minutes at 90° C. In this case, the anisotropy is permanent and must arise from the location of the crosslinks which are distributed at random within an oriented medium.

There is as yet no evidence that the density of crosslinking of a long-chain polymer is affected by either its degree of crystallinity or stress in a chain. All isoprene units in a rubber specimen are equally likely to become crosslinked and the average molecular weight M_c between successive crosslinked units cannot depend on the chain orientation. One possible explanation of the observed anisotropy is that the effectiveness of such links may be different. In an unoriented molecule, the chain will be doubled back on itself a number of times and some links will be formed between units of the same molecules. These will produce closed loops, with little effect on the elastic properties of the material. In a stretched polymer molecule the probability of such closed loops being formed is considerably reduced, whereas in a compressed polymer molecule this probability is increased. The effect of such loops will be to stabilize the oriented structure initially present. Nevertheless one would expect some degree of relaxation when the effect of entanglements is eliminated by heating or swelling. In fact, a crosslinked oriented rubber when swollen in a good solvent which is subsequently evaporated or displaced returns to its initial (oriented) dimension, indicating the absence of any internal stresses due to chain entanglements. That no appreciable relaxation takes place may be as-

cribed to chain scission.   Although irradiation of rubber results primarily in crosslinking, presumably by side chain fracture, some main chain fracture of C—C bonds may be expected to arise.   In an unstressed chain such fractures would have a chance to re-form, and no permanent effect would be noticeable. In a stressed chain fractured bonds would be less likely to recover in this manner and the radicals formed as the result of such breaks would be likely to link themselves to other chains where no such stresses are present.   This stress relaxation phenomenon, which occurs in other polymers, would also account for the observed difference between polymers which crosslink and those which degrade: the latter usually have bulky side chains which cause internal stresses in the molecule.

In conformity with this view, a more highly irradiated rubber (40 Mrad) shows less anisotropy in its mechanical properties, possibly due to the larger number of radiation induced fractures which allow stress relaxation to occur.

The comparison of G values for crosslinking by electron irradiation, and for pile radiation, confirms the conclusion previously reached that crosslinking depends only on the energy absorbed and not on the type of radiation or its intensity.   The G value obtained is only one-third of that observed in the crosslinking of paraffins and this would tend to disprove the view recently advanced that crosslinking arises from the presence of unsaturated C=C bonds which predominate in rubber and are almost completely absent in polyethylene.

SUMMARY

Smoked sheet rubber, previously oriented in the calendering process, was crosslinked by exposure to 2 Mev high energy electrons in the absence of vulcanizing agents.   Even after annealing, the resultant rubber showed anisotropic elastic properties, having a high elastic modulus and a low elongation at break in the direction of orientation.   It is suggested that radiation in addition to crosslinking causes main chain fracture and stress relaxation in stressed molecular chains.   The G value for crosslinking (1.05) by electron irradiation agrees well with that (1.1) previously found by elastic measurements of pile irradiated rubber.

ACKNOWLEDGMENT

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A NEW METHOD FOR DETERMINING THE VULCANIZATION CHARACTERISTICS OF RUBBER COMPOUNDS *

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INTRODUCTION

During vulcanization, a rubber compound passes from the plastic to the elastic state. Examination of the course of the vulcanization curve shows two factors of particular importance: (1) the time at the processing temperature for scorching to set in, and (2) the time at vulcanization temperature to reach the optimum state of cure. Of these two factors, a knowledge of the conditions for optimum vulcanization, on qualitative and technical grounds, is especially essential.

The optimum vulcanization period is normally determined in two separate procedures: (1) the preparation of testpieces which are vulcanized for different periods of time (step cures), and (2) determination of certain characteristic properties of these testpieces.

First of all, static tests are made on the testpieces, for instance of the modulus, tear resistance, tensile strength, hardness and elasticity all at normal and elevated temperatures. Also dynamic properties such as damping and E-modulus are measured in order to help fix the optimum cure of the material. Other methods such as determination of the equilibrium swelling of the samples, are also used[1].

The method of determining the best cure by step cures is not very satisfactory because a great many testpieces must be processed in order to fix the course of the vulcanization curve. Therefore a method was sought which would permit the continuous measurement of one or more characteristic properties on one sample during the process of vulcanization. In this way, the course of the vulcanization curve and the conditions of the optimum cure can be determined. Such a test method must be applicable in the plastic as well as in the elastic region and at the temperature of vulcanization. Static test methods were practically ruled out because large irreversible deformations are associated with their application. It seems possible, however, to apply dynamic test methods, wherein a deformation produced in one phase would have no effect in the next phase.

Dynamic test methods for defining the elastic properties of vulcanizates were described by H. Roelig, and their usefulness explained by him and other authors[2-8]. In the Roelig method of testing (Figure 1) a test sample, usually under precompression load, is subjected to an alternating load. A beam of light, activated with the aid of two rotational mirrors, is deflected by the alter-

nating mechanism; vertical movement is proportional to deformation and horizontal to load. The beam of light describes a true hysteresis loop on a plane, with load on the horizontal and strain on the vertical axis. The area of the damping loop corresponds to the absolute damping; the ratio of the area under the damping loop to that of the energy triangle under the ellipse gives
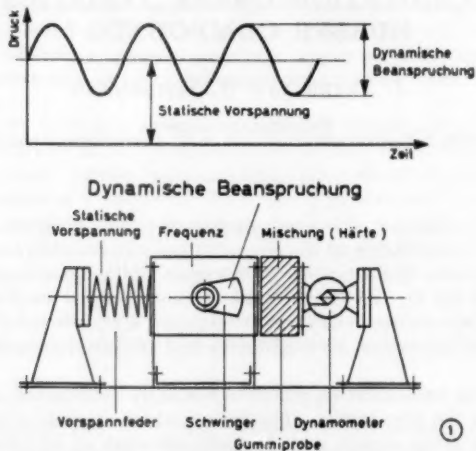
FIG. 1.—Apparatus for measuring damping. Roelig system. Druck = pressure. Zeit = time. Dynamische beanspruchung = dynamic load. Statische Vorspannung = static preload. Frequenz = frequency. Mischung (Härte) = composition (hardness). Vorspannfeder = prestress spring. Schwinger = vibrator. Dynamometer = dynamometer. Gummiprobe = rubber testpiece.

per cent damping; the slope of the damping ellipse gives the dynamic hardness (spring constant). Corresponding measurements on vulcanizates subjected to pretension were described by R. Ecker[9].

METHOD OF MEASUREMENT

Measurement of the course of vulcanization curves involves characterizing vulcanizates as well as unvulcanized compounds and all intermediate stages. For this reason, measurements under tension or compression seemed not too promising. In order to attain a maximum of gripping friction and a minimum of irreversible deformation it was found best to make measurements on rubber vulcanizates under shear at about the zero point of distortion. Measurements made by Ellegast and Juffa on the reaction rate of Vulkollan under other loading conditions, carried out parallel to our investigations, will be reported separately.

In the work at hand, a testpiece is clamped in the apparatus, subjected to a dynamic shearing deformation and the resisting force of the sample is measured. In the case of an unvulcanized compound, as a result of the plastic deformation, only a relatively small force is observed, but in case of a hard vulcanizate, a decidedly larger force is transmitted (corresponding to its higher shear modulus). This is apparent from Figure 2. As is easily seen, it is not only possible to measure the force transmitted by the testpiece—a measure-
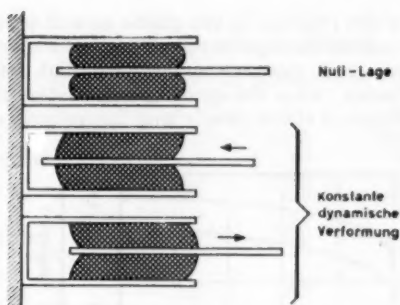
Fig. 2.—Principles of the measuring arrangement and deformation process with unvulcanized compounds and with vulcanizates. Null-Lage = zero deformation. Konstante dynamische verformung = constant dynamic deformation. Weitere gegebene Kräfte = transmitted forces; large in case of vulcanizates and small in unvulcanized mixtures.

ment of the shear modulus—but also to measure the damping. The curves for damping and for shear modulus have an inverse relation. In the soft range the damping is quite high and the shear modulus is very small, while the relations are reversed in case of a vulcanized sample. Since both values—damping and shear modulus—are of equal value in estimating the state of vulcanization, only the shear modulus was determined for this work because in this way the test procedure was greatly simplified. The arrangement of the apparatus is shown in Figure 3.
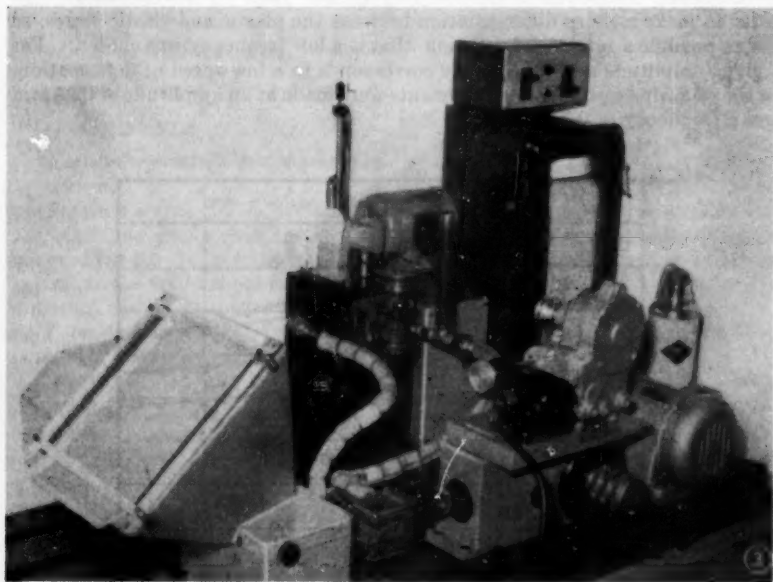
Fig. 3.—Arrangement of apparatus for measuring optimum cure.

In order to follow the relations in the plastic as well as in the elastic range it was necessary to consider the dependence of the plastic-elastic behavior on the speed of deformation. Soft materials subjected to high rates of deformation may react as hard bodies (when the speed of deformation is greater than the velocity of flow). Figure 4 shows clearly that the velocity dependence for an
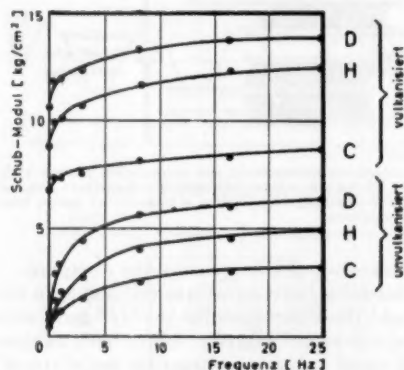
Fig. 4.—Dependence of the shear modulus of unvulcanized compounds and of vulcanizates on rate of deformation. Ordinate is shear modulus (kg/cm²) and abscissa is frequency of vibration, cps.

unvulcanized compound is considerably greater than for a vulcanizate. In order to make a sharp differentiation between the plastic and elastic states, as low as possible a rate of deformation, that is a low frequency was chosen. For a given amplitude a low frequency corresponds to a low speed of deformation. In the following examples measurements were made at an amplitude of 0.25 mm and a frequency of 0.5 cps.
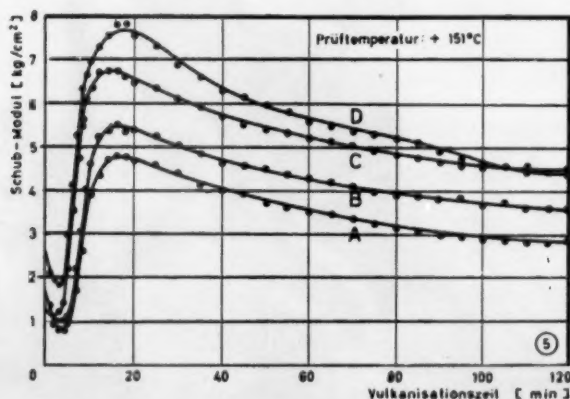
Fig. 5.—The course of vulcanization for natural rubber compounds, with and without fillers. Tested at 151° C. The ordinate is shear modulus (kg/cm²) and the abscissa is time of vulcanization (minutes).

ILLUSTRATIVE APPLICATIONS

Natural rubber, unfilled and with various fillers.—The compounds were:

	A	B	C	D
Smoked sheet	100.0	100.0	100.0	100.0
Zinc oxide (active)	5.0	5.0	5.0	5.0
Sulfur	2.5	2.5	2.5	2.5
Vulkacit CZ*	0.5	0.5	0.5	0.5
Stearic acid	1.0	1.0	1.0	1.0
Barite (heavy spar)	—	50.0	—	—
Carbon black (inactive)	—	—	50.0	—
HAF black	—	—	—	50.0
Paraffin	0.5	0.5	0.5	0.5
Age Resistor, PAN**	1.0	1.0	1.0	1.0

* N-Cyclohexyl-benzothiazolyl-2-sulfenamide.
** Phenyl-1-naphthylamine.

Figure 5 shows the values obtained with the above compounds, measured at 151° C. The reversion, typical of natural rubber when the optimum cure is exceeded is clearly indicated. It is well known that the course of the vulcanization curve is strongly dependent upon the accelerator used.

Cold rubber, unfilled and with various fillers.—The compounds used here were:

	E	F	G	H
Cold rubber	100.0	100.0	100.0	100.0
Zinc oxide (active)	5.0	5.0	5.0	5.0
Sulfur	1.8	1.8	1.8	1.8
Vulkacit CZ	1.3	1.3	1.3	1.3
Stearic acid	1.0	1.0	1.0	1.0
Barite	—	50.0	—	—
Carbon black (inactive)	—	—	50.0	—
HAF black	—	—	—	50.0
Paraffin	0.5	0.5	0.5	0.5
Age Resistor, PAN	1.0	1.0	1.0	1.0
Naftolen ZD*	—	5.0	5.0	5.0

* A paraffin—containing mineral oil product.

Figure 6 shows the values obtained with these compounds when tested at 151° C. The graphs show the absence of the reversion shown with natural rubber, and the curves take another course. While natural rubber shows a definite optimum, the cold rubber compounds show a slow post vulcanization after the optimum cure is reached.

Polychloroprene compounds, unfilled and with various fillers.—Here the compounds of interest were:

	J	K	L
Polychloroprene	100.0	100.0	100.0
Zinc oxide (active)	4.0	4.0	4.0
Magnesium oxide (extra light)	3.0	3.0	3.0
Vulkacit NP*	0.5	0.5	0.5
Stearic acid	1.0	1.0	1.0
Barite	—	50.0	—
Carbon black (inactive)	—	—	50.0
Paraffin	0.5	0.5	0.5
Age Resistor PAN	1.0	1.0	1.0

* A triazine derivative.
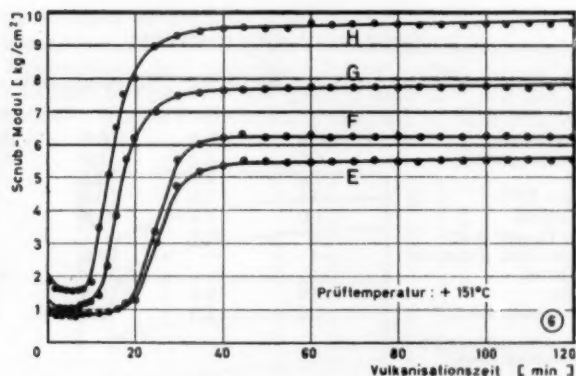
Fig. 6.—The course of vulcanization for cold rubber compounds, with and without fillers. Tested at 151° C.   Coordinates are as in Figure 5.

Figure 7 gives results of tests at 151° C on the above compounds.   The course of the vulcanization curves appears quite similar to that for the cold rubber compounds if one disregards the enhanced susceptibility to vulcanization and the consequent faster curing.   Also with these compounds in contrast to those with natural rubber, no reversion is shown.

Natural rubber compounds with various sulfur and accelerator contents.—The natural rubber Compound B with Barite and Vulkacit CZ was made with three different sulfur levels:

	B	M	N
Smoked sheet	100.0		
Zinc oxide (active)	5.0		
Sulfur	2.5	3.5	4.5
Vulkacit CZ	0.5		
Stearic acid	1.0		
Barite	50.0		
Paraffin	0.5		
Age resister PAN	1.0		
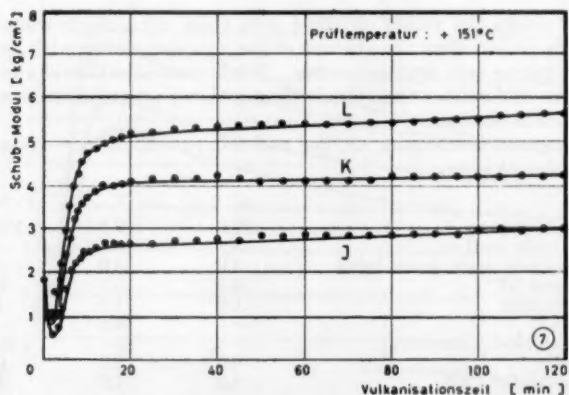
Fig. 7.—The course of vulcanization for polychloroprene compounds, with and without fillers. Tested at 151° C.   Coordinates are as in Figure 5.
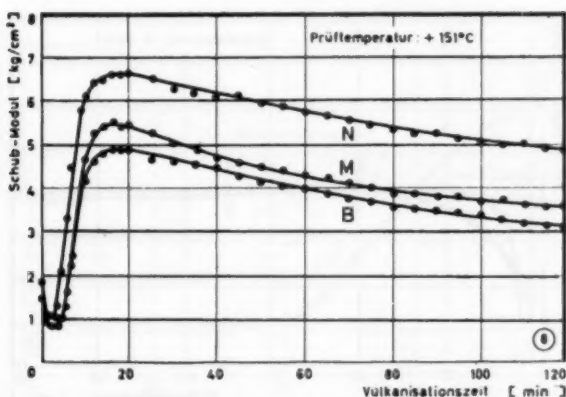
Fig. 8.—The course of vulcanization for natural rubber compounds with Vulkacit CZ and various amounts of sulfur. Temperature 151° C. Coordinates are as Figure 5.

Figure 8 gives data taken at 151° C on the resulting compounds. The shear modulus is increased perceptibly by increase in sulfur content, yet the speed of vulcanization is not particularly changed thereby. The influence of the accelerator on the course of the vulcanization curve is clearly shown here. The same compounds as above, but with 0.5% Vulkacit thiuram show a quite different course, but the dependence on sulfur content is much the same. Figure 9 shows this effect in the following compounds:

	O	P	Q
Smoked sheet	100.0		
Zinc oxide (active)	5.0		
Sulfur	2.5	3.5	4.5
Vulkacit thiuram*	0.5		
Stearic acid	1.0		
Barite	50.0		
Paraffin	0.5		
Age Resistor PAN	1.0		

* Tetramethylthiuram disulfide.
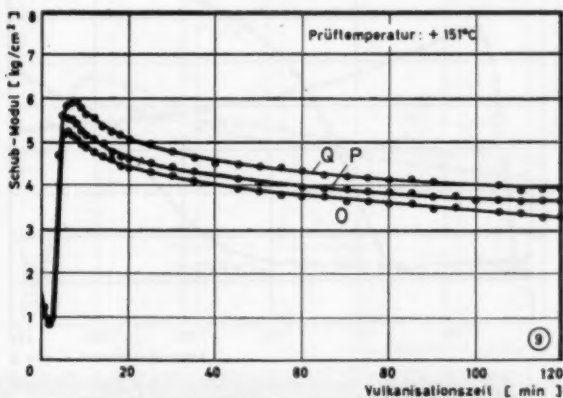
Fig. 9.—The course of vulcanization for natural rubber compounds, at 151° C, with Vulkacit thiuram and various amounts of sulfur. Coordinates are as in Figure 5.
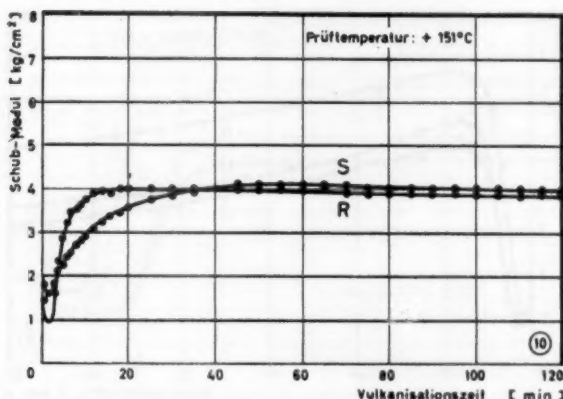
FIG. 10.—The course of vulcanization for natural rubber compounds, without sulfur, but with Vulkacit thiuram and dicumyl peroxide, respectively. Tests at 151° C. Coordinates are as in Figure 5.

Quite a different course for the vulcanization curve is shown for sulfurless cures, both in the presence of Vulkacit thiuram and dicumyl peroxide.   In these cases, the curves show similarity to those for synthetic rubber.   Figure 10 shows the curves for the following mixtures, tested at 151° C:

	R	S
Smoked sheet;	100.0	100.0
Zinc oxide (active)	5.0	—
Vulkacit thiuram	3.0	—
Di-Cup 40 C*	—	4.0
Stearic acid	1.0	—
Barite	50.0	50.0
Paraffin	0.5	0.5
Age Resistor PAN.	1.0	1.0

* 40% Dicumyl peroxide in calcium carbonate.
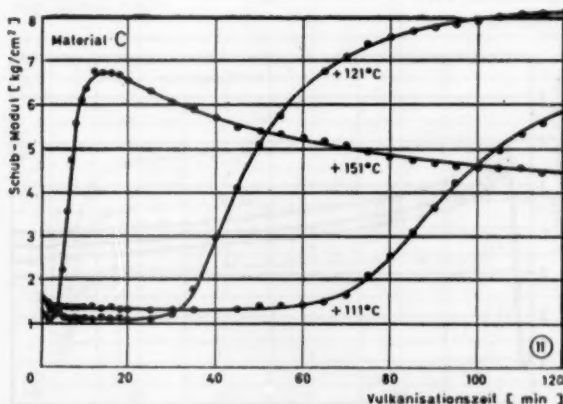
FIG. 11.—The course of vulcanization for a natural rubber—inactive carbon black compound, with Vulkacit CZ, at different temperatures.   Coordinates are as in Figure 5.
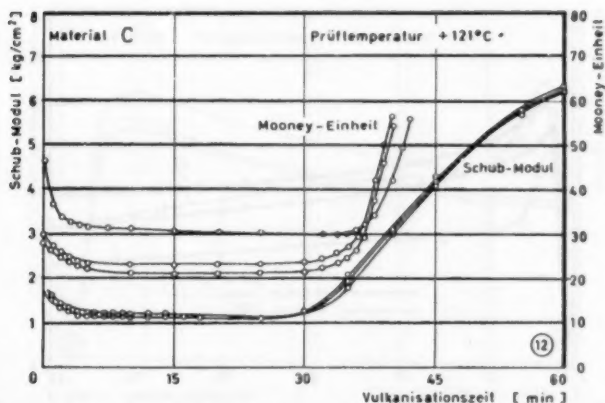
Fig. 12.—Comparison of the rate of vulcanization measured at 121° C, with Mooney values at the same temperature. The ordinates are (1) Shear modulus (kg/cm²) and (2) Mooney units. The abscissa is time of vulcanization (minutes).

Dependence of the course of vulcanization on temperature.—The previously shown curves were all for measurements taken at 151° C. It is possible to determine the vulcanization curves at other temperatures. In Figure 11 are given curves for Compound C taken at different temperatures. Compound C contained inactive carbon black and Vulkacit CZ. These curves show clearly the variations of the course of the curves with temperature. The lower part of the curve for 121° C is quite similar to the curves secured for the same compound with the Mooney apparatus at 121° C. This is shown in Figure 12.

AGREEMENT WITH VALUES OBTAINED BY THE STEP-CURE PROCESS

The dynamic shear modulus is somewhat comparable to the tensile modulus. The values for shear modulus given in the preceding data compare favorably
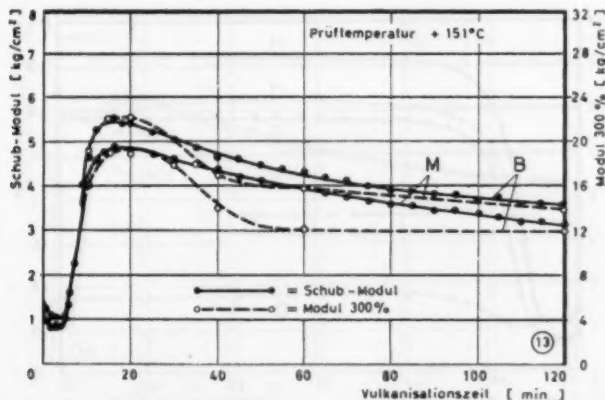
Fig. 13.—Agreement of shear moduli measured at 151° C, with the 300% moduli measured on step-cured samples. Natural rubber compounds B and M were used. The ordinates are (1) Shear modulus and (2) 300% modulus (kg/cm²). The abscissa is time of vulcanization (minutes).
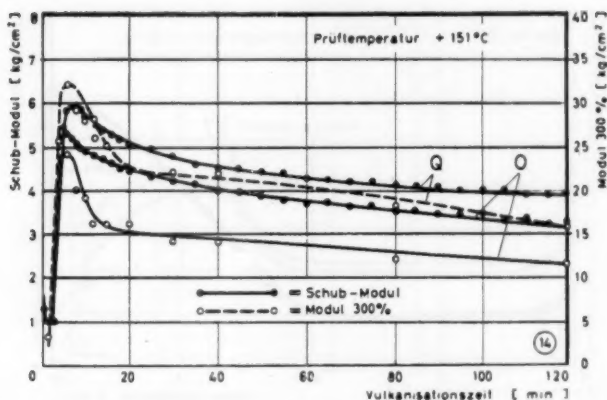
Fig. 14.—Agreement of shear modulus values measured at 151° C, with 300% moduli of step-cured samples of natural rubber compounds O and Q. Coordinates are as in Figure 13.

with corresponding tensile moduli. Without discussing the subject of which method shall be used for determining the optimum cure, it is evident that the values obtained (above) are comparable with the values of the moduli (at 300%). The agreement is shown in the data for Compounds M, B, Q, O, G, and H as set forth in Figures 13, 14 and 15. The agreement is especially apparent in the characteristic course of the curves in Figures 13 and 14.

REPRODUCIBILITY

The test data obtained with the method here described are quite reproducible. Figures 16 and 17 show test data obtained with Compound C. Figure 16 shows data obtained by three different persons on the same mixture, while
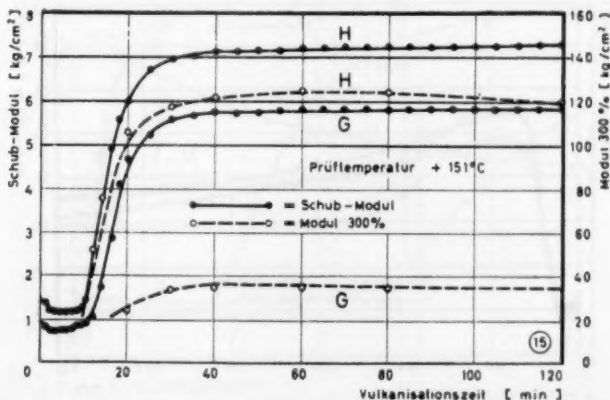
Fig. 15.—Agreement of shear modulus values measured at 151° C, with the 300% moduli on step-cured cold rubber mixtures G and H. Coordinates are as in Figure 13.
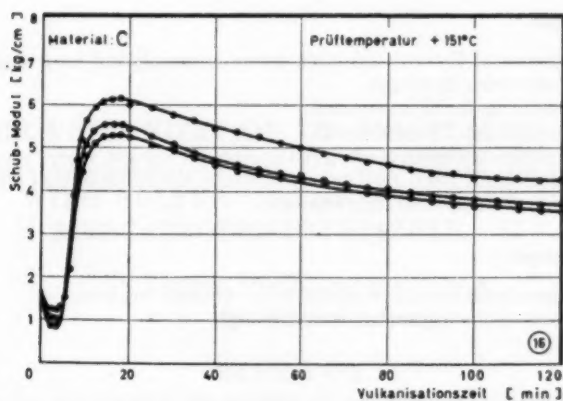
Fig. 16.—Natural rubber compound C measured by three different persons. Temperature 151° C. Coordinates are as in Figure 5.

Figure 17 shows data obtained by one person on the compound prepared by three different operators. Good reproducibility can be noted in the curves.

SUMMARY

The complete course of the vulcanization curve is obtained by measuring the values of the dynamic shear modulus during a period while the test sample is held at the vulcanization temperature. The measurements are made about the position of zero distortion. The curves are in good agreement with those obtained by a step-cure method, and scorch data agree well with those obtained with the Mooney apparatus. The method has the following advantages and disadvantages.
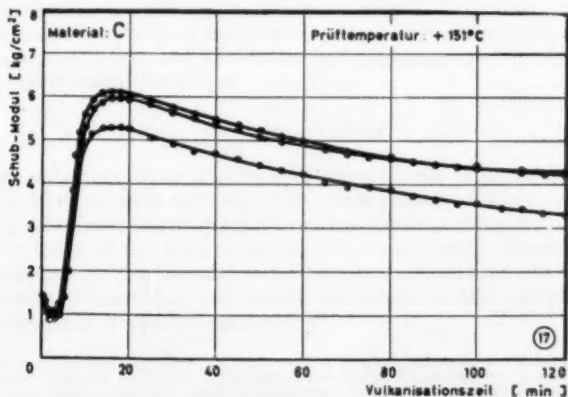
Fig. 17.—Natural rubber compound C prepared by three different persons, using the same raw materials and same milling time and procedures. Coordinates are as in Figure 5.

A. *Advantages*

   1) The course of the vulcanization curve is established on a single sample without curing in stages.
   2) Minimum material is required.
   3) The test is quickly performed.
   4) Good reproducibility is observed.
   5) The unit lends itself readily to automatic recording so that one man can easily operate several instruments.

B. *Disadvantages*

   1) The apparatus should be operated by trained workers.
   2) The cost of the apparatus is rather high.

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THE VULCANIZATION OF ELASTOMERS. 13.
THE VULCANIZATION OF NATURAL RUBBER
WITH SULFUR IN THE PRESENCE OF
MERCAPTOBENZOTHIAZOLE. II *

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INTRODUCTION

Recently[1] we reported the kinetics of mercaptobenzothiazole-accelerated sulfur vulcanization of natural rubber from an investigation limited to mixes containing, in addition to sulfur and zinc oxide, mercaptobenzothiazole or its zinc salt. Among other things we discovered that the decrease in concentration of sulfur in such mixtures, as well as crosslinking measured by reciprocal equilibrium swell, were first order reactions and, what is more essential, that they are processes of equal rate. A further important result was the finding that mercaptobenzothiazole and zinc benzothiazolyl mercaptide had the same accelerating effect. The velocity constants for sulfur decrease and of crosslinking increase were independent of the amount of added accelerator at constant temperature provided, of course, that a minimum amount of mercaptobenzothiazole or its zinc salt, precisely, the amount consumed during vulcanization was added. This quantity is temperature dependent.

Now it is generally known that the physical properties of vulcanizates containing mercaptobenzothiazole or other thiazoles as accelerators can be improved by adding zinc salts of fatty acids or, if zinc oxide is present, by using the corresponding fatty acids. We have therefore extended our investigations to include mixtures containing zinc stearate in addition to sulfur, zinc oxide and mercaptobenzothiazole, and have investigated more thoroughly the kinetics of the decrease of sulfur and accelerator and the increase of crosslinking under different experimental conditions.

EXPERIMENTAL

The investigations were again carried out with pale crepe natural rubber extracted for 48 hours with acetone. The mixes contained, each time, 3.2 g sulfur, 4.07 g zinc oxide and varying amounts of mercaptobenzothiazole and zinc stearate in 103 g of the total mixture. We have already described in detail the preparation of the vulcanizates, their extraction, and the quantitative determination of free sulfur and unused accelerator in the extracts, as well as the determination of equilibrium swelling[2].

RESULTS AND DISCUSSION

The kinetics of the decrease of sulfur and accelerator, and increase of crosslinking.—The mercaptobenzothiazole-accelerated vulcanization of natural rubber with sulfur in the presence of zinc stearate was studied in mixes containing 3.2 g sulfur, 2.09 g mercaptobenzothiazole (molar ratio S_8 : mercaptobenzothiazole $= 1:1$), 4.07 g zinc oxide and 3.0 g zinc stearate. Experiments were conducted over a temperature range of 90° to 140° C. In Table I results of the quantita-

TABLE I

Sulfur Cure of Natural Rubber in the Presence of Mercapto-benzothiazole, Zinc Oxide, and Zinc Stearate

Composition of mix: 3.20 g sulfur, 2.09 g mercaptobenzothiazole, 4.07 g zinc oxide, 3.00 g zinc stearate, and 90.64 g natural rubber. Vulk.-Z. = vulcanization time. Ungeb. S = free sulfur. Unverbr. Beschl. = unused accelerator. Benzol = benzene.

90° C

Vulk.-Z. [min]	100	200	300	400	500	600	800	1000	∞
% Ungeb. S	83.8	68.7	54.2	38.0	26.8	19.2	10.6	5.4	
% Unverbr. Beschl.		92.7	90.3	88.5	86.2	84.7	82.7	82.1	81.0
$1/Q_t$ (Benzol)	0.0585	0.183	0.236	0.2665	0.2855	0.2965	0.309	0.3115	0.316

100° C

Vulk.-Z. [min]	40	80	120	180	240	300	400	500	∞
% Ungeb. S	100.6	83.0	69.6	45.2	30.8	19.3	9.0	4.6	
% Unverbr. Beschl.		95.3	89.8	87.7	86.2	83.1	80.7	80.5	79.0
$1/Q_t$ (Benzol)		0.155	0.218	0.260	0.283	0.298	0.305	0.306	0.309

110° C

Vulk.-Z. [min]	20	40	70	80	100	150	200	300	∞
% Ungeb. S	98.0	70.2	57.6	45.2	30.7	16.7	9.3	3.0	
% Unverbr. Beschl.		93.2	92.2	90.1	88.5	84.4	83.9	79.3	81.0
$1/Q_t$ (Benzol)	0.0415	0.184	0.236	0.270	0.285	0.298	0.305	0.306	0.315

120° C

Vulk.-Z. [min]	10	20	30	40	60	80	110	150	∞
% Ungeb. S	89.3	65.7	52.2	43.9	24.7	17.4	8.0	3.6	
% Unverbr. Beschl.		93.7	92.2	88.4	85.8	82.5	81.8	81.0	81.0
$1/Q_t$ (Benzol)	0.0513	0.183	0.226	0.246	0.278	0.285	0.283	0.278	0.294

130° C

Vulk.-Z. [min]	10	15	20	25	30	40	50	60	∞
% Ungeb. S	98.4	72.3	57.8	47.3	40.9	22.0	13.1	6.3	
% Unverbr. Beschl.		95.5	93.8	90.6	89.5	85.2	82.6	80.8	80.0
$1/Q_t$ (Benzol)		0.1805	0.217	0.241	0.255	0.277	0.287	0.291	0.295

140° C

Vulk.-Z. [min]	10	15	20	25	30	35	40	50	∞
% Ungeb. S	65.1	42.1	27.5	14.4	8.8	5.3	4.6	3.6	
% Unverbr. Beschl.	93.0	87.7	84.1	82.1	81.5	80.1	79.2	79.0	79.0
$1/Q_t$ (Benzol)	0.1495	0.221	0.242	0.251	0.254	0.249	0.255	0.2455	0.258

tive analyses of the extracts are assembled. Uncombined sulfur and recovered accelerator are entered in per cent of the initial amounts.

The sulfur disappearance once again proceeds according to the first order, for when the log of the uncombined sulfur is plotted against the vulcanization time, straight lines are obtained (Figure 1). It is noteworthy, however, that an induction period occurs which increases as the temperature falls, and amounts to about 120 minutes at 90° C. At the start of vulcanization, it causes a slight deviation in sulfur disappearance from a first order course. It must be stressed,
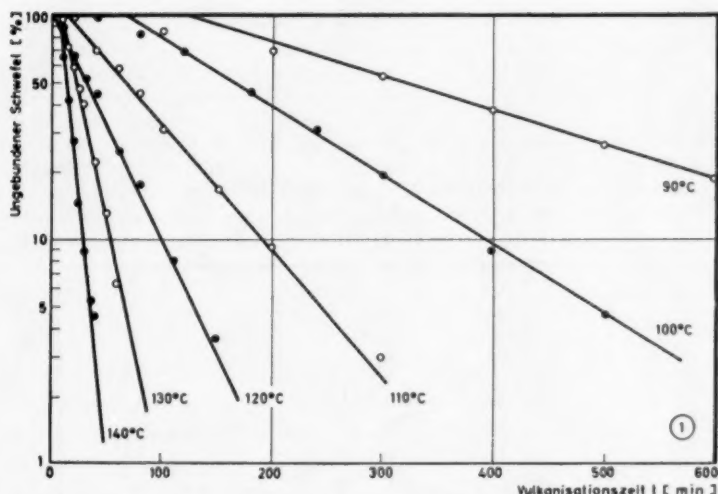
Fig. 1.—First order plots of sulfur disappearance in MBT accelerated sulfur curing of natural rubber in the presence of zinc oxide and zinc stearate. Vulkanisationszeit = vulcanization time.

however, that the induction period is also dependent on the experimental mixing conditions. It will be proportionately smaller as the time of milling is lengthened and the milling temperature is raised.

A comparison of the rate constants k_z^I, calculated from the slopes of the straight lines in Figure 1, with corresponding values for sulfur-diminution rate constants in the absence of zinc stearate (Table II) shows that the stearate induces a considerable rise in the reaction rate. One finds that at 90° C the rate constants differ by about a factor of 50. With rising temperature, this factor diminishes markedly so that at 140° C it amounts only to 8. From this it is seen that vulcanization in the presence of stearate displays a different activation energy from that arrived at from the temperature dependence of sulfur

TABLE II

COMPILATION OF RATE CONSTANTS AND ACTIVATION ENERGIES E_A

Zusammensetzung der Mischung = composition of mixture, Kautschuk = rubber.

Zusammensetzung der Mischung	3.20 g Schwefel 2.09 g Mercaptobenzothiazol 4.07 g Zinkoxyd 90.64 g Kautschuk		3.20 g Schwefel 2.09 g Mercaptobenzothiazol 4.07 g Zinkoxyd 3.00 g Zinkstearat 90.64 g Kautschuk		
Vulk.-Temp. ° C.	$k_S I \cdot 10^2$ [min^{-1}]	$k_Q I \cdot 10^2$ [min^{-1}]	$k_S I \cdot 10^2$ [min^{-1}]	$k_B I \cdot 10^2$ [min^{-1}]	$k_Q I \cdot 10^2$ [min^{-1}]
90			0.33	0.30	0.50
100			0.70	0.68	1.14
110	0.06	0.06	1.31	1.29	2.47
120	0.15	0.15	2.60	2.79	5.28
130	0.46	0.51	4.95	4.79	7.62
140	1.23	1.18	9.20	9.20	17.70
150	2.70	2.79			
E_A[kcal/Mol]	30.5	30.5	19.5	19.5	20.5

disappearance in cures taking place in the presence of mercaptobenzothiazole and zinc oxide alone. Thus the relationships are completely changed.

Figure 2 (ordinate: $\log k_S{}^I$ or $\log k_Q{}^I$; abscissa: $1/T \cdot 10^3$) represents the temperature dependence of the rate constants in cures accelerated by mercaptobenzothiazole and zinc oxide, in the presence or absence of zinc stearate (Curves I and II, respectively). From the slope of Curve I an activation energy of 29.5 kcal/mole is obtained, whereas a considerably smaller value of 19.5 kcal/mole is derived from Curve II. The decline in activation energy for the conversion of sulfur occasioned by the addition of zinc stearate is hence
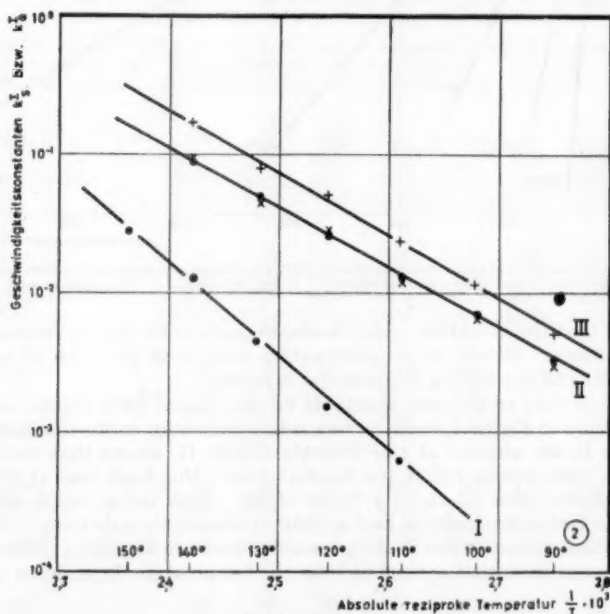
FIG. 2.—The temperature dependence of the rate constants. Curve I: Sulfur disappearance in the presence of mercaptobenzothiazole and zinc oxide. Curve II: Sulfur (O) and accelerator diminution (X) in the presence of mercaptobenzothiazole, zinc stearate and zinc oxide. Curve III: Reciprocal equilibrium swelling in the presence of mercaptobenzothiazole, zinc stearate and zinc oxide. Vulkanisationszeit = vulcanization time.

considerable and must certainly be regarded as proof of a catalytic effect of the stearate. Since this effect, as will be explained later, is connected with the presence of mercaptobenzothiazole, it can be presumed that the effective accelerator is composed of mercaptobenzothiazole and zinc stearate.

Of great interest, naturally, is the answer to the question as to how the altered kinetic relationships of sulfur-diminution influence crosslinking, of which the reciprocal values of the equilibrium swellings of the vulcanizates (T = constant) are a measure. An analysis of the change in the reciprocal equilibrium swelling, $1/Q_t$, during vulcanization as a function of vulcanization time shows that the crosslinking can once again be described as a first order reaction. This is seen from Figure 3 [ordinate (logarithmic): $1/Q_\infty - 1/Q_t$;

abscissa: vulcanization time t in minutes]. At all temperatures straight lines are obtained with great accuracy.

In determining $1/Q_\infty$ it must be pointed out that in the experiments discussed here the values of $1/Q_t$ for vulcanizates having a very long curing time were in general constant, so that a special determination of $1/Q_\infty$ by extrapolation of the values for equilibrium swelling could be dispensed with. In other cases $1/Q_\infty$ was obtained by plotting log $1/Q_t$ against the reciprocal vulcanization time and extrapolating the curves thus obtained to intersect the ordinate. The reversion of crosslinking observed in certain cases was not taken into consideration when $1/Q_\infty$ was derived[1].
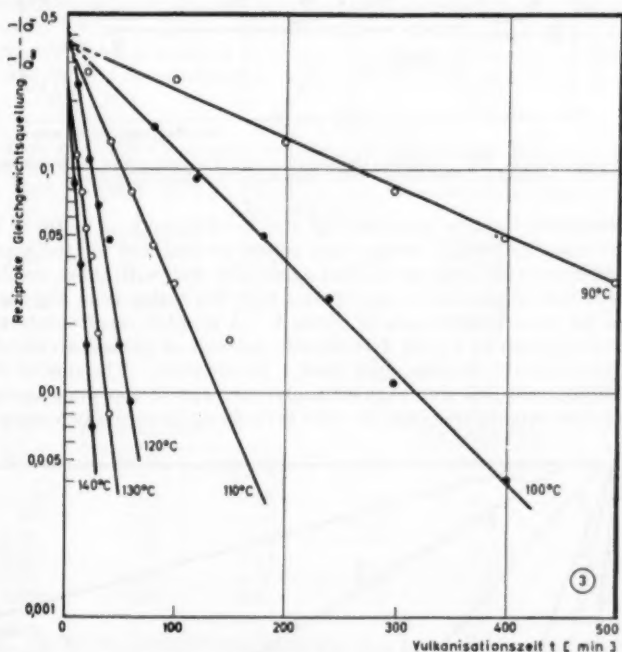
FIG. 3.—First order reciprocal equilibrium swelling in mercaptobenzothiazole-accelerated sulfur curing of natural rubber in the presence of zinc stearate and zinc oxide.

A calculation of the rate constant $k_Q{}^I$ from the slope of the straight lines in Figure 3 shows then—and this must be especially emphasized—that reciprocal swelling and sulfur disappearance are not equal rate processes, which, however, was always the case in the absence of zinc stearate. For $k_Q{}^I$ is in each instance larger than $k_S{}^I$ each time by an approximately constant factor of about 2. The activation energy of the network forming reaction was found, from the temperature dependence of the rate constant $k_Q{}^I$ (Curve III in Figure 2), to be 20.5 kcal/mole. Gee and Morrell[3] have already pointed out that in compounds containing zinc stearate, the first order increase in combined sulfur and the crosslinking reaction, which could also be described as first order reactions according to their experiments, are not equal rate processes. For the compounds
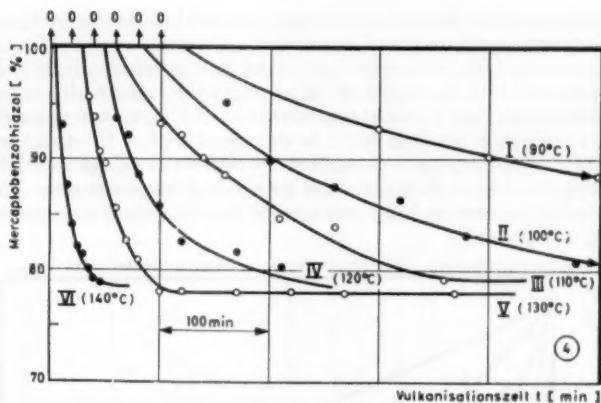
Fig. 4.—Disappearance of MBT accelerator during sulfur cure of natural rubber in the presence of zinc stearate and zinc oxide. Vulkanisationszeit = vulcanization time.

they investigated the rate constants k_Q^I and k_S^I differed by a factor of 3. For the crosslinking activation energy they found 18 kcal and for the reaction of sulfur with rubber 20 kcal, values that agree very well with those we obtained.

The per cent diminution in accelerator with the curing time is given by the third line for each temperature in Table I. A graphic representation of the relationships is seen in Figure 4 (ordinate: amount of unused accelerator still present, in per cent; abscissa: cure time, t, in minutes). The sum of the mercaptobenzothiazole and zinc benzothiazolyl mercaptide was once again determined without establishing how the sum is made up from the two components.
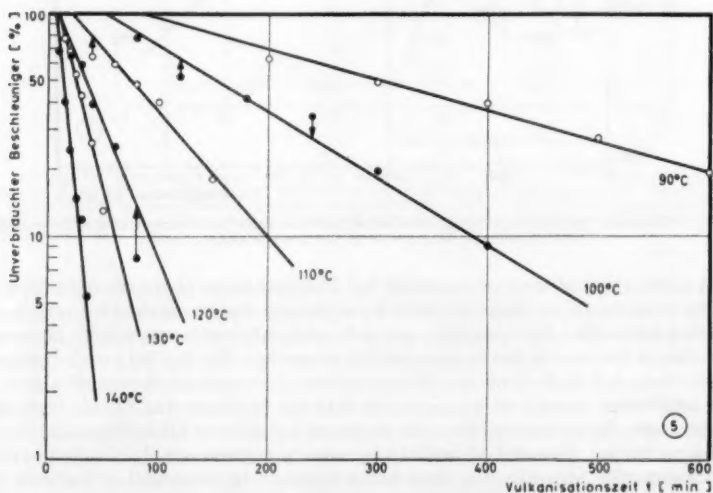
Fig. 5.—First order disappearance of accelerator (maximum accelerator consumption = 100). Vulkanisationszeit = vulcanization time.

A closer look at Figure 4 will show that the maximum diminution in accelerator is practically independent of the temperature. At each vulcanization temperature, eventually, the same terminal concentration of the accelerator occurs. It varies between 78 and 82 per cent of the initial quantity, i.e., under the experimental conditions chosen, about 0.4 g of mercaptobenzothiazole was used up. It may be mentioned right here that a change in the amount of added stearate does not affect this result.

In this vulcanization, too, the disappearance of the accelerator is tied in with the sulfur reaction; for, from Curve V in Figure 4 it can be seen that after about 100 minutes at 130° C no more accelerator is used up. In reality the sulfur diminution is practically at an end after this time (cf. Table I).

A kinetic analysis of accelerator diminution, made more difficult, certainly, by the relatively small amount used up, viz., about 20 per cent of the amount put in, and by the proportionately not inconsiderable analysis error (1–2 per

TABLE III

COMPILATION OF RATE CONSTANTS FOR SULFUR DIMINUTION (k_S^I) AND NETWORK FORMATION (CROSSLINKING) (k_Q^I) AT 120° C FOR VARIOUS INITIAL AMOUNTS OF ZINC STEARATE AS A FUNCTION OF THE MERCAPTOBENZOTHIAZOLE CONTENT (MBT)

1 g Zinkstearate			2 g Zinkstearate		
MBT g	$k_S^I \cdot 10^2$ [min^{-1}]	$k_Q^I \cdot 10^2$ [min^{-1}]	MBT g	$k_S^I \cdot 10^2$ [min^{-1}]	$k_Q^I \cdot 10^2$ [min^{-1}]
2.09	1.59	3.77	0.53	0.84	1.38
			1.06	1.38	2.34
			1.59	1.98	3.65
			2.09	2.26	4.42
			3.17	2.25	4.60
			4.23	2.19	4.47

3 g Zinkstearate			5 g Zinkstearate		
MBT g	$k_S^I \cdot 10^2$ [min^{-1}]	$k_Q^I \cdot 10^2$ [min^{-1}]	MBT g	$k_S^I \cdot 10^2$ [min^{-1}]	$k_Q^I \cdot 10^2$ [min^{-1}]
0.792	1.10	2.32	1.32	2.13	2.75
1.585	2.24	4.26	2.64	3.43	4.77
2.09	2.60	5.28	3.96	4.76	5.98
3.17	3.78	6.39	5.28	6.58	7.54
3.96	3.52	6.57	6.60	6.50	8.07
4,755	3.83	6.53	7.92	6.32	7.88

cent), will, however, demonstrate that this is a first order reaction, as can be seen from Figure 5. From the calculated rate constants k_B^I it is evident that sulfur loss and accelerator consumption are equal rate processes (cf. also Curve II in Figure 2 and Table II). On the basis of the constant limiting value of 20 per cent diminution in the accelerator and the rate equivalence of the two processes it follows that in each stage of the reaction, for every five S_8 molecules one molecule of mercaptobenzothiazole is simultaneously converted.

Experimental results with variation of the quantity of added mercaptobenzothiazole.—In order to be able to investigate the influence of the amount of mercaptobenzothiazole on the kinetics of this vulcanization, compounds were cured at 120° C, containing, besides sulfur and zinc oxide (each time 3.2 and 4.07 g, respectively, in 103 g of mix), a certain amount of zinc stearate, as well as increasing quantities of mercaptobenzothiazole. There was 1, 2, 3, or 5 g of zinc stearate per 103 g of total mixture. Table III gives the calculated velocity constants.
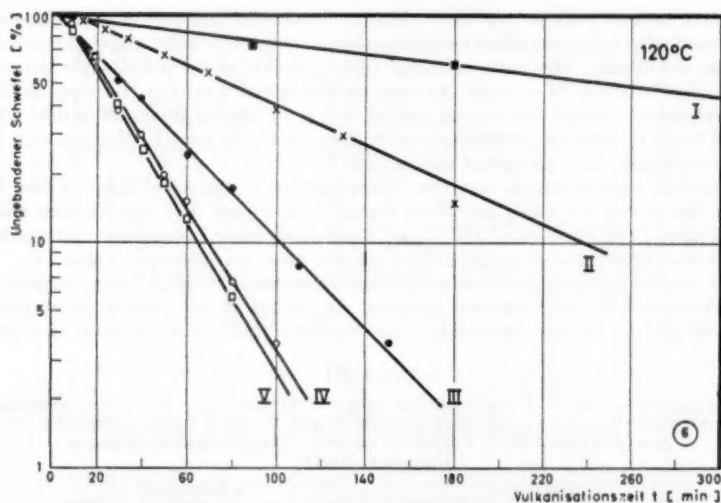
Fig. 6.—First order sulfur diminution for different proportions of added MBT in the presence of 3 g zinc stearate per 103 g of mixture. Molar ratio, zinc stearate to MBT—Curve I = 0; Curve II = 1:1; Curve III 1:2.5; Curve IV = 1:4; Curve V = 1:6. Vulkanisationszeit = vulcanization time.

The reaction order of sulfur diminution or of crosslinking increase is not affected by a change in the initial amount of accelerator, since both processes go once again according to the first order.   Figures 6 and 7, in which the ordinates (logarithmic) are, respectively, the uncombined sulfur in per cent of the
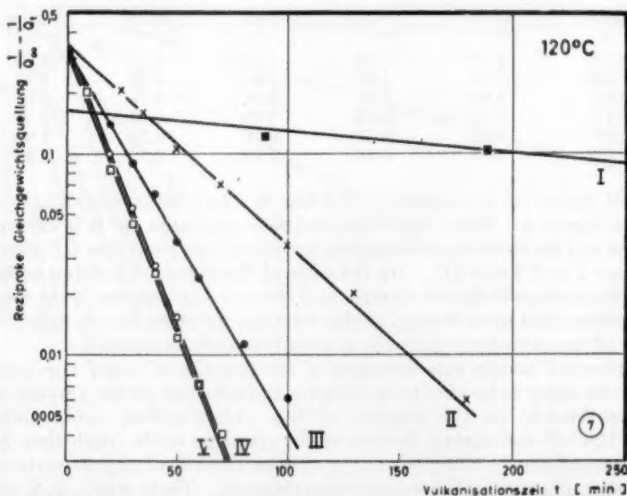
Fig. 7.—Reciprocal equilibrium swell, first order, at various proportions of added MBT in the presence of 3 g zinc stearate per 103 g mix. Molar ratio, zinc stearate to MBT—Curve I = 0; Curve II = 1:1; Curve III = 1:2; Curve IV = 1:4; Curve V = 1:6.

initial quantity and the difference $(1/Q_\infty - 1/Q_t)$, and the abscissa curing time t in minutes, demonstrate this fact for compounds containing 3 g zinc stearate and various quantities of mercaptobenzothiazole. The individual straight lines, however, show differences in their slopes, i.e., the mercaptobenzothiazole content of the compounds has an influence on the rate constants of sulfur disappearance and crosslinking.

When $k_S{}^I$ or $k_Q{}^I$ (ordinate) are plotted against the initial mercaptobenzothiazole (abscissa) there is observed (Figure 8), up to an initial molar ratio of mercaptobenzothiazole:zinc stearate $= 4:1$, a rise in the rate constants with the increase in $k_S{}^I$ being linear, whereas the plot for $k_Q{}^I$ curves away from the ordinate axis. Both curves intersect the ordinate axis at $k = 0.15 \times 10^{-2}$ min^{-1}. This value is equivalent to the rate constants for disappearance of sulfur and crosslinking during cure without added zinc stearate, conditions under which both processes had proved to be of the same rate, while the rate
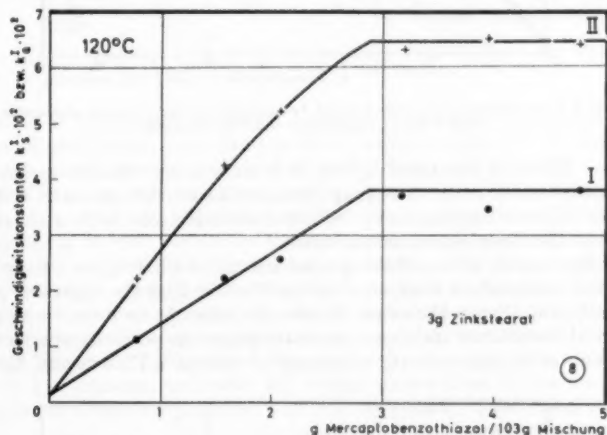
FIG. 8.—The dependence of the rate constants $k_S{}^I$ (Curve I) and $k_Q{}^I$ on the amount of added accelerator (in the presence of 3 g zinc stearate per 103 g of mix).

constants were independent of the mercaptobenzothiazole content ($T = $ constant)[1]. However, when the mercaptobenzothiazole content goes beyond the molar ratio $4:1$, the rate constants remain unchanged. Only when there is a further increase in stearate content do the increased accelerator dosages effect a renewed rise in rate constants, and then only until the initial molar ratio $4:1$ is once again reached. The relation between the rate constant $k_S{}^I$ (ordinate) and the amount of accelerator in grams (abscissa) in compounds of varying stearate content is portrayed in Figure 9. All rate constants fall on one straight line, which then always goes over into a course parallel to the abscissa whenever, at a given stearate content, the initial molar ratio mercaptobenzothiazole:zinc stearate exceeds $4:1$ (Curve portions b, c and d). Whether this is a stoichiometric ratio must be determined by experiments conducted at other cure temperatures.

Now it is very remarkable that when $k_Q{}^I$, the rate constant of the network formation is plotted against the increase in amount of accelerator with varying additions of zinc stearate, no linear dependence is observed. This is shown in
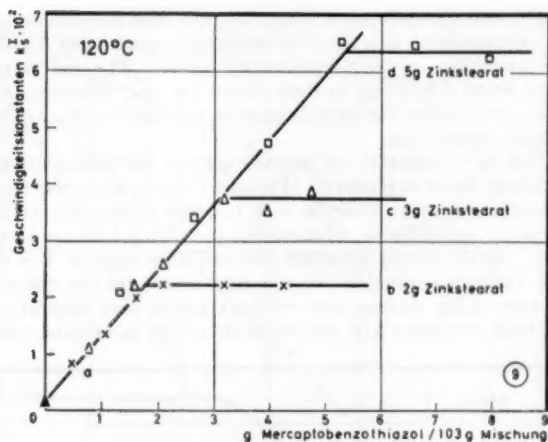
FIG. 9.—Dependence of the rate constant $k_S{}^I$ on the proportion of added accelerator with different quantities of added zinc stearate.

Figure 10.   The rate constants $k_Q{}^I$ do, it is true, attain maximum values also with an initial molar ratio of mercaptobenzothiazole:zinc stearate = 4:1, but they lie on a curve turning away from the ordinate axis with a considerable scattering in the three experimental series.

As for the degree of crosslinking attained, of which $1/Q_\infty$ is a measure, the experimental values show that, considering the fact that the degree of mastication is surely not always the same, despite the attempt to preserve as uniform experimental conditions (mixing and mastication) as possible, one can nevertheless speak of an approximate constancy of values.   This means, then, that
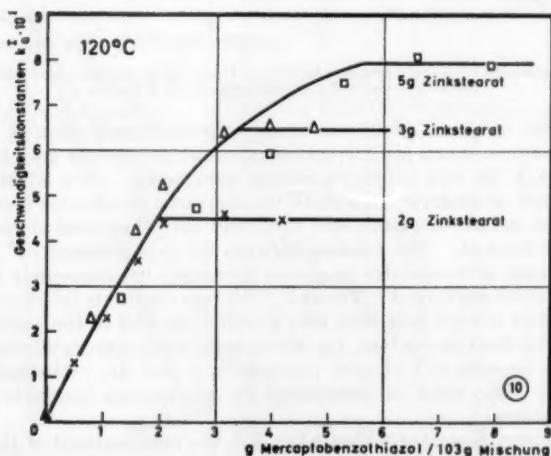
FIG. 10.—The dependence of the rate constants $k_Q{}^I$ on the quantity of added accelerator, with different portions of added zinc stearate.
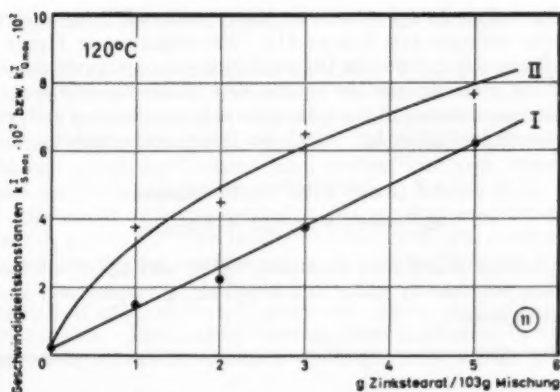
FIG. 11.—The dependence of the rate constant $k_S{}^I$ (max) (Curve I) or $k_Q{}^I$ (max) (Curve II), on the amount of added zinc stearate.

the number of linkage points formed during vulcanization is independent of the quantity of accelerator, provided the same curing temperature is used. These relationships have already been pointed out by H. E. Adams and B. J. Johnson[4]. The effect of mercaptobenzothiazole thus is due exclusively to an acceleration in curing, but is without noticeable influence on the final degree of crosslinking.

Influence of stearate content on mercaptobenzothiazole-accelerated sulfur cures. —The relations shown in Figures 9 and 10 between the rate constants $k_S{}^I$ or $k_Q{}^I$ and the initial amount of mercaptobenzothiazole in compounds with varying stearate contents now make it possible to discuss the relationships existing between the proportion of zinc stearate and the maximum attainable rate constants $k_S{}^I$ (max) and $k_Q{}^I$ (max). Figure 11 (abscissa: zinc stearate content in g per 103 g of mixture; ordinate: $k_S{}^I$ (max)) shows that, in the range investigated, a linear dependency exists (Curve I) between $k_S{}^I$ (max) and the stearate
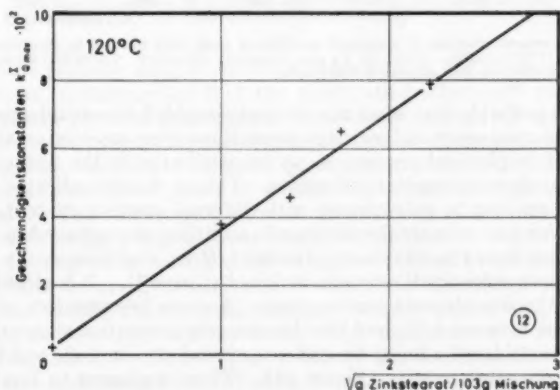
FIG. 12.—The dependence of the rate constant $k_Q{}^I$ (max) on the square root of the amount of added zinc stearate.

content.   The values for k_Q^I (max), on the other hand, lie on a curve turning away from the ordinate axis (Curve II).   Nevertheless, as Figure 12 shows, there is also linear dependence for the maximum rate constants for crosslinking k_Q^I (max) if one plots against the square root of the stearate content.   Thus one has, for the dependence of the maximum rate constants of sulfur disappearance and network formation k_Q^I (max), on the stearate content, the following two expressions:

$$k_S^I \text{ (max)} = k_S^I(0) + a \cdot c_{\text{stearate}} \tag{1}$$

$$k_Q^I \text{ (max)} = k_Q^I(0) + b \, c_{\text{stearate}} \tag{2}$$

In the equations, a and b are constants, $k_S^I(0)$ and $k_Q^I(0)$ are the rate constants for disappearance of sulfur and crosslinking respectively in vulcanizations without stearate[5].
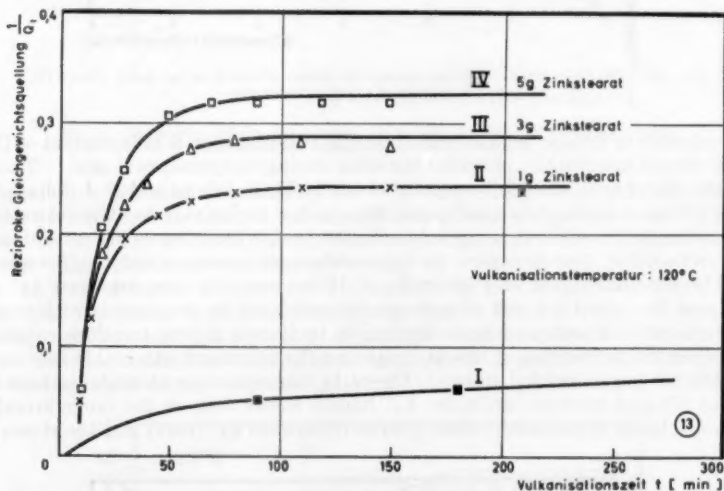
FIG. 13.—Increment observed in reciprocal equilibrium swell with increase in cure time.   Curve I: 0 g zinc stearate $(1/Q = 0.166)$.   Curve II: 1 g zinc stearate in 103 g mix.   Curve III: 2 g zinc stearate in 103 g mix.   Curve IV: 3 g zinc stearate in 103 g mix.

It is very probable that when zinc stearate is added to vulcanizates containing sulfur as curing agent and mercaptobenzothiazole as accelerator, the ensuing improvement in physical properties can be attributed to the formation of an increasing number of crosslinkage points.   This is clearly indicated by measurements of swelling in vulcanizates with different stearate content, but with constant sulfur and mercaptobenzothiazole addition, as portrayed in Figure 13 (abscissa: cure time t in minutes; ordinate: $1/Q_t$).   For comparison the curve for stearate-free vulcanization is also included (Curve I).   It is clear that $1/Q_\infty$ increases as the zinc stearate content rises.   A closer investigation of the functional relation between $1/Q_\infty$ and the zinc stearate proportion shows that in the range being considered a linear dependence exists between $1/Q_\infty$ and the square root of the stearate quantity (Figure 14).   Thus, analogous to Equation (2), one has:

$$1/Q_\infty = (1/Q_\infty)_0 + b' \cdot \sqrt{c_{\text{stearate}}}$$

whereby $(1/Q_\infty)_0$ signifies the equilibrium swell of the stearate-free vulcanizate for $t \to \infty$.

Barton and Hart[6] have attempted to derive a relationship between the number of crosslinkage points formed and the amount of added fatty acid (lauric acid) from measurements of conventional modulus values (200% elongation) of quite thoroughly cured vulcanizates.   They came to the conclusion that modulus values improve as the lauric acid content increases, but remain constant above a critical concentration of lauric acid.   Adding lauric acid, therefore, also brings about an improvement in the physical properties of the vulcanizates, which proves that the results obtained with the accelerator system mercaptobenzothiazole plus zinc stearate are in no wise limited to this combination.

The zinc salts of other carboxylic acids also exert an influence on the speed of this vulcanization.   Exploratory investigations conducted by us with compounds containing equimolar amounts of formic acid, acetic acid and pro-
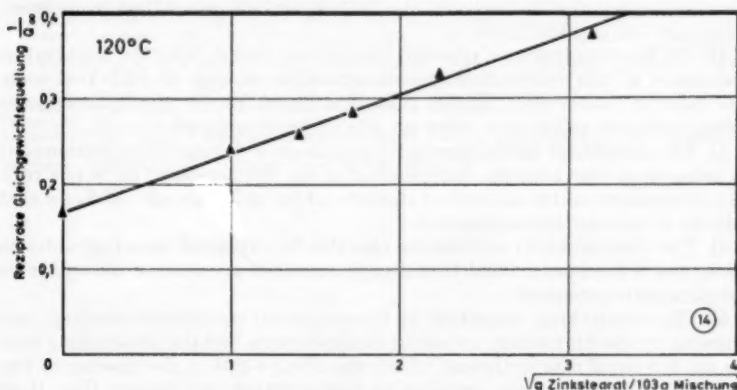
Fig. 14.—Dependence of reciprocal equilibrium swell, $1/Q$, on square root of initial amount of zinc stearate.

pionic acid or palmitic acid, when the composition of the mixture was otherwise the same, demonstrated that the accelerating effect and the attendant improvement in physical properties of the vulcanizate are all the more pronounced when the molecular weight of the fatty acid in question is greater[7].

The experimental results obtained up to now give no indication as to how the increase in number of points of crosslinkage occurs through the action of zinc stearate.   This could result either from a shifting of the ratio of intra- to intermolecular bridge bonds to favor intermolecular bonds, or from a favorable formation of mono sulfur and disulfur as against polysulfur bonds.   Consideration must also be given to additional bonds of a different nature.   Besides, in such situations the experimental results must be reckoned with, whereby the crosslinking reaction proceeds more swiftly in the presence of stearate than does the diminution in sulfur.   This points to the fact that the uncombined sulfur still available toward the end of the reaction evidently does not enter any longer into network formation, but is used up in a side reaction.   Armstrong, Little, Doak[8] have examined the possibility that with cures in the presence of

zinc oxides and fatty acids, thiols and zinc mercaptides might be produced, which could react with free sulfur to form disulfides and zinc sulfides:

$$F—S—Zn—S—R + S \longrightarrow F—S—S—R + ZnS$$
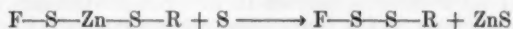
Such a reaction, in fact, makes it understandable how sulfur can become combined, even though the degree of crosslinkage undergoes no further change. But whether it really corresponds basically to what actually takes place cannot be decided as yet.

SUMMARY

The vulcanization of natural rubber with sulfur, using mercaptobenzothiazole as accelerator in the presence of zinc stearate, was investigated. The results were as follows:

1) When natural rubber is cured with sulfur in the presence of zinc oxide and mercaptobenzothiazole, as well as zinc stearate, one observes, with the first order diminution of sulfur concentration, an induction period that grows longer as the cure temperature falls.

2) For the disappearance of sulfur there is calculated, from the temperature dependence of the rate constants, an activation energy of 19.5 kcal/mole. This value is considerably smaller than that found for the mercaptobenzothiazole-accelerated sulfur cure when no zinc stearate is present.

3) The percentage loss in mercaptobenzothiazole during vulcanization is, in the presence of zinc stearate, independent of the temperature; there is a reaction, independent of the amount of stearate added of 5 molecules of S_8 for each molecule of mercaptobenzothiazole.

4) The diminution in accelerator can also be explained as a first order reaction, and it becomes evident that disappearance of accelerator and sulfur are equivalent-rate processes.

5) The crosslinking, measured by the reciprocal equilibrium swelling, goes according to the first order, yet sulfur disappearance and the crosslinking reaction are not equal rate processes, which was always true in the absence of zinc stearate. In each case the crosslinking rate constants are greater than those for the decrease in sulfur.

6) For the activation energy of network formation, we calculated, from the temperature dependence of the rate constants of the reciprocal equilibrium swelling, 20.5 kcal/mole.

7) When the stearate content is constant, there is a linear relationship between $k_S{}^I$, the rate constant for sulfur diminution, and the given amount of mercaptobenzothiazole, up to an initial molar ratio of mercaptobenzothiazole: stearate = 4:1. Increases in accelerator proportion beyond this initial ratio cause no further rise in the rate constants.

8) The rate constants of the crosslinking reaction also increase with increasing proportion of mercaptobenzothiazole (stearate portion remaining constant), until the initial molar ratio of mercaptobenzothiazole:zinc stearate = 4:1 is reached. Nevertheless, the relationship is not linear.

9) There is a linear relationship between the amount of zinc stearate in the vulcanizate and the maximum sulfur-loss rate constants $k_S{}^I$ (max).

10) The maximum rate constants of the network forming reaction $k_Q{}^I$ (max) are proportional to the square root of the stearate content.

11) The number of crosslinkage points formed is independent of the quantity of mercaptobenzothiazole, when the stearate content is constant.

12) The number of crosslinking points formed increases, however, along with increasing stearate content, and is proportional to the square root of the stearate content.

The investigations will be continued.

ACKNOWLEDGMENT

We wish to thank Prof. W. Scheele for furthering the present work, and for his numerous valuable suggestions. Fräulein I. Roser helped us in the carrying out of many experiments.

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[1] Lorenz and Echte, *Kautschuk u. Gummi* **10**, WT23 (1957).
[2] If the mixes contain greater amounts of mercaptobenzothiazole, it is recommended that the aqueous solutions obtained after conversion of the free sulfur, with KCN, to KSCN, be extracted by shaking with ethyl acetate, in order to remove any mercaptobenzothiazole that might be present, because the latter would also be involved in the titration with AgNO₃ (cf. loc. cit. Reference 1).
[3] Gee and Morrell, Rubber Chem. & Technol. **25**, 454 (1952).
[4] Adams and Johnson, *Ind. Eng. Chem.* **45**, 1539 (1953).
[5] We also tried to see whether zinc stearate influences the reaction rate of sulfur in rubber, in the absence of mercaptobenzothiazole. For this the loss in sulfur at 130° C was investigated for two compounds, one of which contained only sulfur and zinc oxide (3.2 g and 4.07 g respectively per 100 g of mix), and the other an added 4 parts by weight of zinc stearate. For the loss in sulfur, according to the first order in both cases, the following rate constants were obtained: $0.31 \cdot 10^{-2}$ min⁻¹, or, in the presence of zinc stearate $0.15 \cdot 10^{-2}$ min⁻¹. This makes it clear that zinc stearate alone does not exert an accelerative influence, but rather, retards—if only to a slight degree.
[6] Barton and Hart, *Ind. Eng. Chem.* **44**, 2444 (1952).
[7] Later on we shall report in detail the quantitative results obtained when other fatty acids or their salts are added.
[8] Armstrong, Little and Doak, *Ind. Eng. Chem.* **36**, 628 (1944).

THE THERMAL VULCANIZATION OF
SYNTHETIC RUBBER *

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INTRODUCTION

At the 11th general meeting of the Deutsche Kautschuk-Gesellschaft in 1938 H. Hagen read a paper on the plastication of Buna rubber and made the following statement: "If Buna is heated with exclusion of air it becomes gradually harder, e.g., cyclization, crosslinking or 'vulcanization' takes place without the addition of sulfur." In 1944, E. Weinbrenner and B. Scheurle of the Technical Application Department of the Buna Works in Schkopau were investigating the vulcanization of Buna S with benzothiazolyl disulfide. During this work it was confirmed that certain Buna types can be vulcanized merely by simple thermal treatment. This finding however could not be fully utilized due to the existing war situation. To distinguish this process from the customary vulcanization procedure with sulfur and accelerator, Weinbrenner and Scheurle introduced the term "thermovulcanization" which will be used throughout this paper. In investigations of the vulcanization of various synthetic rubbers we have again been attracted to this phenomenon and have carried out a few series of experiments with the aim of determining the effect of thermovulcanization on various synthetic rubbers and of learning more exactly the properties of the vulcanizates produced.

THE BEHAVIOR OF DIFFERENT BUNA TYPES
ON THERMOVULCANIZATION

Natural rubber, without the addition of sulfur or accelerators, softens under the influence of heat either in the presence of air or under its most perfect exclusion. Synthetic rubbers soften by heat only if air is present. The plasticizing of natural rubber by thermal treatment is being utilized to some extent. Thus, for example, so-called "softened rubber" is natural rubber thermally plasticized[1,2]. With some Buna rubber types, thermal plasticization has attained, as is well known, a great significance[3,4]. Contrary to natural rubber however, Buna rubber does not soften if air or oxygen is effectively excluded. Some Buna types under this condition, on the other hand, thermovulcanize to soft rubber.

The following Schkopau Buna types were studied with respect to their behavior in thermovulcanization: Buna S 3, Buna SS 3, Buna S 4, Buna S 4/L, Buna S 4/T, Buna N, Buna NW, and Buna 85; also smoked sheets were studied. Some characteristics of the aforesaid Buna rubbers are found in Table I.

Each material was subjected to step-wise vulcanization from 30 to 480 minutes at different temperatures in a press.

All of the Buna types under investigation could be cured to soft rubber by the thermovulcanization process.   Differences in the susceptibility to thermovulcanization exist, however, among the individual polymers.   Of the emulsion polymers, butadiene-acrylonitrile copolymers (Buna N and Buna NN) show a more intensive thermovulcanizing effect than butadiene-styrene copolymers, the higher styrene-content polymer (Buna SS 3) being vulcanizable in this way only under certain conditions.   The heat plasticized polymers as well as the plastic polymerizates produced by regulated polymerization are slower to thermovulcanize than the corresponding polymerizates with lesser plasticization. The butadiene block polymerizate Buna 85 shows the highest tendency to vulcanization by thermal treatment.   Buna SS 3 and Buna 85 have not been further investigated.

TABLE I

CHARACTERISTICS OF BUNA–TYPES INVESTIGATED

Buna rubber	Monomer components	Per cent bound comonomer, approx.	Temperature of polymerization, °C	Approx. raw plasticity (Defo-hardness)
S 3[1]	Butadiene-Styrene[3]	28	48	3000
S 4[1]	Butadiene-Styrene[3]	28	48	600
S 4/T[1]	Butadiene-Styrene[3]	20	5	600
S 4/L[1]	Butadiene-Styrene[4]	28	48	600
SS[1]	Butadiene-Styrene[3]	50	48	3000
N[1]	Butadiene-Acrylonitrile[3]	25	35	3000
NW[1]	Butadiene-Acrylonitrile[3]	25	35	600
NN[1]	Butadiene-Acrylonitrile[3]	35	30	3000
85[2]	Butadiene[3]	—	80	600

[1] Emulsion polymerizate
[2] Block polymerizate
[3] Stabilized with phenyl-2-naphthylamine
[4] Stabilized with dihydroxydiphenylsulfide

The possible effect of stabilizer on the thermovulcanization was noticed in a comparison of Buna S 4 with Buna S 4/L.   The latter contains dioxydiphenyl sulfide as a stabilizer and shows a greater susceptibility to thermovulcanization than Buna S 4 which is stabilized with phenyl-2-naphthylamine.   Natural rubber (smoked sheets) cannot be vulcanized by the thermovulcanization process, even with the addition of phenyl-2-naphthylamine or dioxydiphenyl sulfide.

In determining what temperatures are adequate for thermovulcanization, based on tensile strength of the vulcanizates, it was found at temperatures from 180 to 200° C for various periods of time that a plateau of good tensile strength values results.   These equal approximately the values of corresponding sulfur-accelerator vulcanizates.   The step-wise heating at still higher temperatures
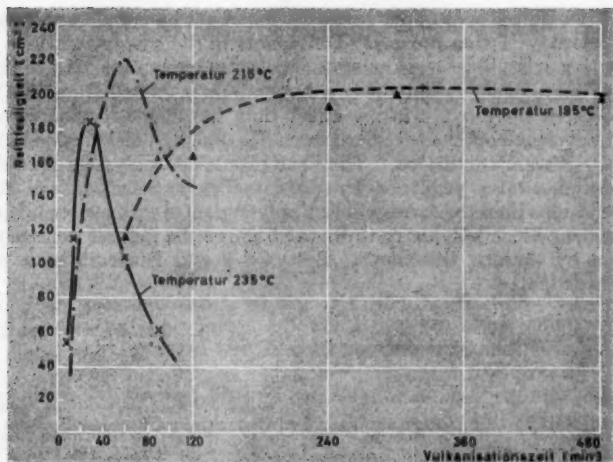
Fig. 1.—Influence of temperature of vulcanization on tensile strength of Buna S 4/T thermovulcanizates Ordinate: tensile strength, kg/cm². Abscissa: vulcanization time, minutes.

(215–235° C) failed to produce this plateau for the butadiene-styrene copolymers. The course of thermovulcanization for the low-temperature polymerizate Buna S 4/T is shown in Figure 1. Besides, at temperatures over 200° C, with more extended time periods, rebound elasticity shows a sharp drop, a sign that rubberlike characteristics at these temperatures are being strongly depressed. Also in the case of the butadiene-acrylonitrile polymerizates, such as Buna NN, a fast drop in resilience is noted at temperatures 215° and 235° C, although the tensile strength maintains a certain plateau. We have therefore
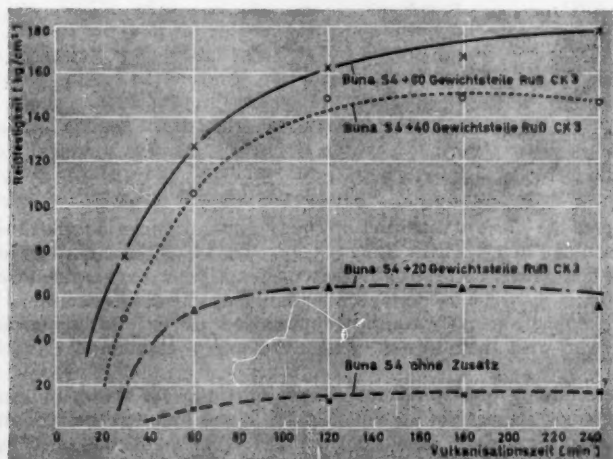
Fig. 2.—Effect of active carbon on the course of thermovulcanization of Buna S 4. Ordinate: tensile strength, kg/cm². Abscissa: vulcanization time, minutes.

limited our investigations of thermovulcanizates to products which have been vulcanized at 195° C.

PROPERTIES OF THE THERMOVULCANIZATES

Vulcanization carried out at 195° C with different Buna rubber types which contained no fillers or other additives yielded products of very low tensile strengths. They were somewhat below the already low values of the corresponding sulfur-accelerator vulcanizates. The properties of these fillerless thermovulcanizates have not been investigated in detail. The addition of active carbon has improved the tensile strength and other properties of the vulcanizates. Besides, when adding the active carbon, an accelerating effect on the thermovulcanization was noted. This is shown in Figure 2, for example, with Buna S 4 to which 0 to 60 parts by weight of carbon black CK 3 have been added. Further experiments have shown that zinc oxide has no noticeable influence on tensile strength in case of butadiene-styrene copolymers. On the other hand, somewhat improved values were obtained for butadiene-acrylonitrile copolymers.

COMPARISON OF THERMOVULCANIZATES WITH NORMAL VULCANIZATES

Experimental series with Vulkazit AZ.—We have therefore added to the different Buna S rubbers 45 parts by weight of CK 3 black and in the case of Buna N, Buna NW and Buna NN in addition to this also 10 parts by weight of zinc oxide. From these compounds thermovulcanizates were prepared and compared with vulcanizates from corresponding simple compounds with sulfur and Vulkazit AZ accelerator. The composition of the compounds and the results are shown in Table II.

The tensile strength values of thermovulcanizates (I) are in general somewhat lower than those of the sulfur-accelerator containing vulcanizates (II). In some cases however closely corresponding values have been obtained. There is no appreciable difference in the elongation values. The thermovulcanizates were found to be somewhat better, in resistance against tear initiation, the difference however not being significant. The situation is different however in regard to abrasion, rebound elasticity, and surface crack-growth resistance (De Mattia). Here the thermovulcanizates proved definitely better. Especially in the case of butadiene-styrene copolymers plasticized by regulated polymerization (Buna S 4 and Buna S 4/T) very desirable improvements have been noted. The results with Buna S 4/L are not discussed in this connection on account of the different type of stabilization. If the values for normal vulcanizates (II) of Buna S 3 are compared with Buna S 4 and Buna S 4/T, one finds, as may be expected, the more strongly regulated polymerizates clearly lower in rebound, abrasion resistance, and surface crack growth resistance, with the exception of Buna S 4/T which in abrasion resistance practically equals Buna S 3. The rebound elasticity values of thermovulcanizates of Buna S 4 and Buna S 4/T are almost at the same level with those of Buna S 3, and in abrasion and crack growth resistance they are even better than for Buna S 3.

The swelling values for all thermovulcanizates have been found to be larger than those of sulfur-accelerator vulcanizates.

The results of electrical testing as well as tensile strength and elongation data at elevated temperatures (up to 125° C) are not discussed here to any

TABLE II

COMPARISON OF PROPERTIES OF THERMOVULCANIZATES AND SULFUR-VULKAZIT AZ VULCANIZATES (UNAGED VULCANIZATES)

Composition of compounds

	I Thermovulcanizates, parts by weight	II Sulfur-Vulkazit AZ vulcanizates, parts by weight
Polymerisate	100.00	100.00
Carbon black CK 3	45.00	45.00
Zinc white RS		10.00
Sulfur	0 or 10.00 resp.	1.25–2.40[1]
Vulkazit AZ	—	0.15–0.95[1]

Polymer 1	Buna S 3 (2)		Buna S 4 (3)		Buna S 4/L (4)		Buna S 4/T (5)		Buna N (6)		Buna NW (7)		Buna NN (8)	
Initial plasticity (Defo-hardness)	Thermally degraded to 850		550		650		650		2800		600		3100	
Compound	I	II	I	II	I	II	I	II	I	II	I	II	I	II
Vulcanisation, min °C	300/195	100/143	180/195	80/143	60/195	60/143	240/195	50/143	60/195	40/143	120/195	80/143	45/195	40/143
Tensile strength DIN 53 504 Rg. I (kg/cm²)	174	234	172	201	183	198	183	199	205	192	184	213	224	233
Elongation (%) DIN 53 504 Rg. I	550	520	515	495	515	525	505	520	440	400	510	515	470	410
Resistance against tear propagation (Graves) (3. Norm-sheet May 1954) ∥[2]	17.3	14.9	20.1	17.0	17.0	15.9	17.6	16.4	18.1	18.8	21.3	21.3	23.7	22.3
⊥[3]	17.5	14.5	21.6	17.0	17.8	15.0	19.3	16.1	17.8	19.4	23.3	21.9	25.3	22.5
Abrasion (mm³)	65	83	59	99	77	111	51	85	46	72	75	86	61	74
DIN 53 516 (%)[3]	78.3	100	59.6	100	69.4	100	60.0	100	63.9	100	87.2	100	82.4	100
Rebound elasticity DIN 53 512 at 22° C (%)	52	51	48	42	46	42	49	42	41	38	41	34	29	25
DeMattia test, number of flexes — Surface Crack Growth (DeMattia Test) — for degree 1[4]	304.2[5]	65.7	675.6[4]	17.7	260.1	9.9	[a,b]	23.1	98.1	26.7	[a,b]	24.3	[a,b]	23.7
for degree 5	600.9	120.9	828.0	37.2	320.1	19.5		33.9	91.5	36.3		31.5		31.5
Swelling (% by wt.) Extraction naphtha 60–90 at +50° C — 24 hours	114.2	90.7	111.8	84.6	108.1	86.8	100.6	90.9	12.0	10.1	14.3	11.8	4.3	2.4
48 hours	123.6	94.1	114.9	85.3	109.9	91.2	110.4	91.1	14.6	12.6	15.5	13.8	6.7	5.5
96 hours	126.9	94.7	116.3	87.3	102.7	92.1	113.0	94.4	14.9	13.2	16.0	14.2	8.5	7.6

Note: If not otherwise stated, test temperature of +22° C was used for the values obtained.
[1] Varied according to polymer used.
[2] ∥ In the direction of milling; ⊥ Perpendicular to the direction of milling.
[3] Abrasion of II equals 100.
[4] X 10⁴.
[5] Degree 1: First detectable crack development; Degree 10: Specimen practically broken.
[a] At 750 X 10⁴ flexes still no trace of cracks.
[b] Partly (on some specimens) after 750 X 10⁴ flexes still no sign of cracking.
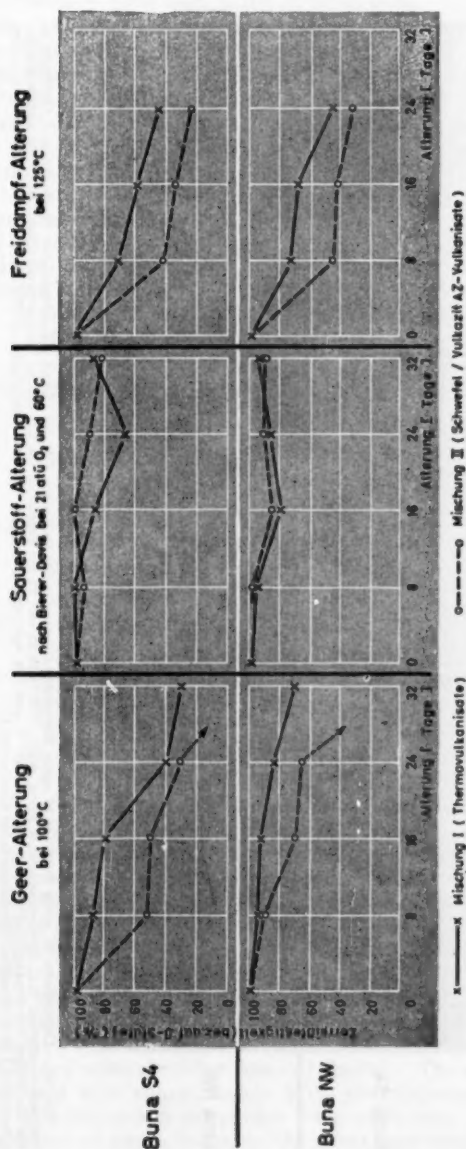
FIG. 3a.—Comparison of aging behavior of some thermovulcanizates (solid line) with sulfur-Vulkazit AZ-vulcanizates (dashed line). Ordinate is tensile strength, kg/cm². Abscissa is time of aging, days.
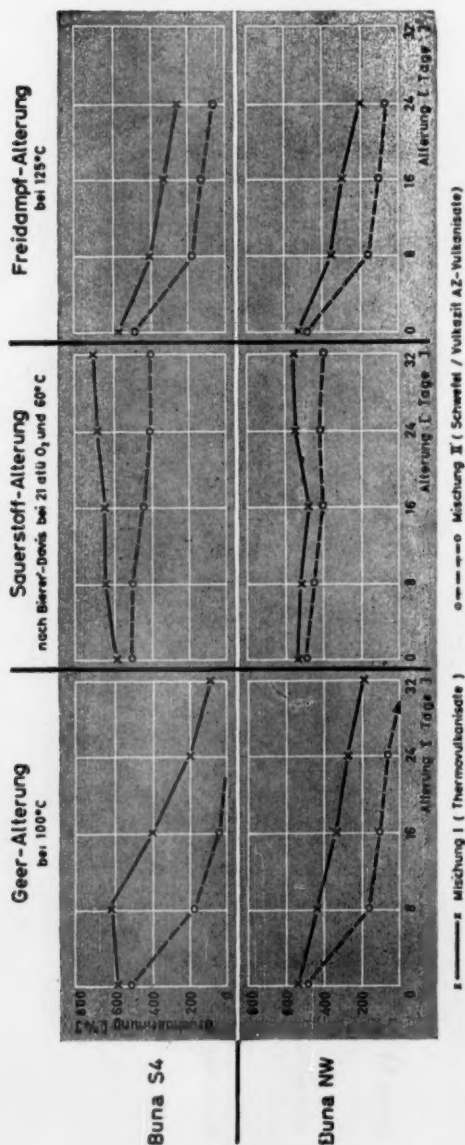
Fig. 3b.—Comparison of aging behavior of some thermovulcanizates (solid line) with sulfur-Vulkasit AZ-vulcanizates (dashed line). Ordinate is ultimate elongation, %. Abscissa is time of aging, days. For both 3a and 3b the graphs on the left are for Geer oven aging at 100° C, the middle graphs are for oxygen bomb aging at 21 atmospheres and 60° C, and the right side graphs are for open steam aging at 125° C. The thermovulcanizate is for Compound I and the sulfur vulcanizate is for Compound II.

length. No differences have been noted in these tests. We also do not discuss here the results of fatigue tests which in general gave somewhat lower values for the thermovulcanizates.

The results of aging tests however deserve closer discussion. The testing of aging resistance was done by exposure to hot air (Geer aging at 100° C), oxygen (Bierer-Davis test at 20 atm oxygen at 60° C), and free steam at 125° C. For Buna S 4 and Buna NW the differences in aging behavior are illustrated graphically in Figures 3a and 3b. In the case of Geer aging and free steam aging, a clear superiority for the thermovulcanizates is apparent. This is especially noticeable in comparing the elongations. In oxygen aging there is no essential difference in the drop of tensile strength in general between the thermovulcanizates and normal vulcanizates. In some individual cases the behavior of normal vulcanizates is even somewhat better than that of thermovulcanizates. In other cases the slight differences turn in the opposite direc-

TABLE III

COMPOSITION OF THERMOVULCANIZATE AND SULFUR–THIURAM
VULCANIZATE COMPOUNDS

Polymer	Buna S 4	Buna S 4/T	Buna NW	Buna S 4	Buna S 4/T	Buna NW	Natural rubber (smoked sheets)
Composition of compound (parts by weight)	I (Thermovulcanizates)			II (Sulfur-thiuram vulcanizates)			
1	2	3	4	5	6	7	8
Polymer	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Carbon black CK 3	45.00	45.00	45.00	45.00	45.00	45.00	45.00
Zinc white RS	—	—	10.00	10.00	10.00	10.00	10.00
Stearic acid	—	—	—	0.50	0.50	0.50	0.50
Phenyl-2-naphthylamine	0 or 1.0, respectively	0 or 1.0, respectively	0 or 1.0, respectively	0 or 1.0, respectively	0 or 1.0, respectively	0 or 1.0, respectively	2.50
Mercaptobensimidazole	0 or 1.0, respectively	0 or 1.0, respectively	0 or 1.0, respectively	0 or 1.0, respectively	0 or 1.0, respectively	0 or 1.0, respectively	1.00
Sulfur	—	—	—	0.30	0.30	0.25	0.45
Vulkazit DM	—	—	—	0.15	0.15	0.15	0.10
Thiuram	—	—	—	1.25	1.30	1.10	0.60

tion. On the other hand, there is an increase in the elongations of thermovulcanizates with increasing time of oxygen exposure, in contrast to the elongations of normal vulcanizates, a phenomenon which in general does not occur in Bierer-Davis aging of synthetic rubber vulcanizates. Also, the Shore hardness and resilience values, which are not discussed here in detail, show a drop for the thermovulcanizates during the oxygen aging test.

Experimental series with thiuram.—In a further series of tests we have compared the rubberlike properties as well as aging resistance of thermovulcanizates and thiuram-sulfur vulcanizates, the elastomers tested being Buna S 4, Buna S 4/T, Buna NW and natural rubber (smoked sheets). The synthetic rubbers used were stabilized with approximately 2.5% phenyl-2-naphthylamine (see also Table I). For this reason compounds were made from them in one case without any addition of antioxidants, in the other case with the addition of phenyl-2-naphthylamine plus mercaptobenzimidazole. The natural rubber was compounded with an amount of phenyl-2-naphthylamine corresponding to that in the synthetic rubbers. The composition of the compounds is given in

TABLE IV

COMPARISON OF PROPERTIES OF THERMOVULCANIZATES AND SULFUR-THIURAM VULCANIZATES (UNAGED VULCANIZATES)

Polymer 1	Buna 8 4		Buna 8 4/T		Buna NW		Natural rubber (smoked sheets) 8
	2	3	4	5	6	7	8
Initial plasticity (Defo-hardness)	690		550		750		1050 (masticated)
Compound	I	II	I	II	I	II	II
Vulcanisation (min./°C)	240/105	60/143	240/105	60/143	180/195	30/143	40/143
Tensile Strength and Elongation							
Tensile strength DIN 53 504 Rg. I (kg/cm²)	201	203	196	199	176	199	235
Elongation (%) DIN 53 504 Rg. I	545	635	600	570	405	520	605
Resistance against Tear-Propagation and Abrasion							
Resistance to tear propagation (Graves) (3. Norm-sheet) (May 1954) ⊥)	21.2 / 20.7	22.3 / 26.8	28.0 / 27.9	24.8 / 26.0	26.0 / 25.4	27.7 / 27.6	15.5 / 22.1
Abrasion DIN 53 516 (mm³) / (%)[3]	80 / 74	108 / 100	57 / 56	102 / 100	86 / 77	110 / 100	121
Rebound Elasticity							
Rebound elast. (%) DIN 53 512 +22°C / +70°C	46 / 47	42 / 46	44 / 57	41 / 45	35 / 44	35 / 46	47 / 50
Surface Crack-Growth (De Mattia)							
De Mattia test, number of flexes for degree 1[3]	Partially >765.0⁴	153.5⁴	Strong Fluctuations	40.2⁴	Partially >765.0⁴	Partially >765.0⁴	86.7⁴

TABLE IV—(Continued)

Polymer 1	Buna S 4		Buna S 4/T		Buna NW		Natural rubber (smoked sheets)
	2	3	4	5	6	7	8
For degree 5	Large fluctuations	307.2	Strong fluctuations Av. > 300.0	142.2	Large Fl.	Large Fl.	233.4
For degree 10	Large Fl.	532.2	Strong Fl.	258.9	Large Fl.	Large Fl.	273.0

Swelling (% by wt.), extraction naphtha 60–90 at +50°C

	2	3	4	5	6	7	8
24 hours	105.3	91.0	108.7	102.2	16.5	15.6	167.2
48 hours	113.9	101.8	113.7	101.2	18.8	18.8	169.7
72 hours	105.1	100.4	114.2	101.6	19.2	21.7	165.7
96 hours	11.6	98.9	112.1	101.9	19.4	19.4	162.9

Koch Bending Test

	2	3	4	5	6	7	8
E-point °C	−52.5	−52.6	−58.8	−56.6	−35.5	−34.8	−62.1
V-point °C	−34.8	−35.8	−38.2	−36.3	−23.4	−22.8	−49.8

Damping

Damping DIN 53 513	Temperature °C	Spring constant kg/cm	Damping %
Buna S 4 (2)	75 / 100 / 86	396 / — / 356	30.8 / — / 30.5
Buna S 4 (3)	75 / 100 / 78	238 / 299 / 297	31.5 / 31.3 / 31.4
Buna S 4/T (4)	75 / 100 / 78	427 / — / 423	35.1 / — / 35.4
Buna S 4/T (5)	75 / 100 / 103	360 / 319 / 319	32.4 / 31.6 / 31.0
Buna NW (6)	— / — / 73	— / — / 524	— / — / 37.4
Buna NW (7)	75 / — / 96	387 / — / 336	37.7 / — / 34.4
Natural rubber (8)	75 / 100 / 121	191 / 185 / 189	22.8 / 21.9 / 21.5

Electrical Properties

Electrical properties Specific resistance KV/mm	2	3	4	5	6	7	8
	5.06 × 10⁷	8.9 × 10⁷	4.37 × 10⁷	9.22 × 10⁸	7.20 × 10⁸	6.85 × 10⁸	1.13 × 10⁸
	1.49	3.38	1.44	3.95	2.84	4.90	5.29

1 = in the direction of milling; ⊥ perpendicular to the direction of milling.
2 Abrasion of II equals 100.
3 Degree 1: First detectable development of cracks; Degree 10: Specimen practically broken.
4 × 10⁸.
5 Natural rubber + 2.5% PBN + 1% MB.

Table III.   As may be seen, the normal vulcanizates are now aimed at having good aging resistance.   The physical and mechanical properties of the unaged vulcanizates are given in Table IV.   The values obtained on unaged vulcanizates are reported only on the compounds containing PBN and MB as there were, naturally, no differences found compared to the antioxidant-free compounds.

The test data for this series have confirmed a number of findings from the Vulkazit AZ test series.   The tensile strength, elongation and the resistance against tear propagation are practically the same for thermovulcanizates and sulfur-thiuram vulcanizates.

Also no basic differences have been noted regarding electrical properties and changes of properties at low temperatures.   The tendency to swell is somewhat higher for the thermovulcanizates as in the Vulkazit AZ test series.   The abrasion resistance of the thermovulcanizates again is definitely better, and for the butadiene-styrene copolymerizates, the room temperature rebound elasticity values were again several points higher than those for the sulfur-thiuram vulcanizates.   On the other hand, the rebound elasticities measured at 70° C show a far-reaching agreement.   The testing of dynamic behavior on the Roelig vibration machine reveals that the generation of heat is clearly lower in all cases for thermovulcanizates.   In the percentage of damping, however, no difference was found between thermovulcanizates and sulfur-thiuram vulcanizates.

A clear difference between thermovulcanizates and sulfur-thiuram vulcanizates exists in the dynamically determined spring constants.   The spring constants of the thermovulcanizates are all clearly higher although this should not be expected from the figures of tensile modulus at 300% elongation or from the Shore A hardness values (see also Table IVa).

The resistance against surface crack growth at a dynamic stress as determined by De Mattia test shows again that the thermovulcanizates are more resistant, though considerable fluctuations exist in the test results.

Furthermore the weather resistance of thermovulcanizates and sulfur-thiuram vulcanizates was investigated (cracking or crazing by light) by means of a method which corresponds closely to the ASTM D-1171-51T procedure. The results are not given here.   The thermovulcanizates based on Buna S 4 and Buna S 4/T have shown a somewhat higher resistance against crack formation than the sulfur-thiuram vulcanizates, e.g., the thermovulcanizates need longer times to develop the first cracks.   Besides, after a given weather exposure, they show in general a smaller number of cracks.   The progression of cracking is slower than with the sulfur-thiuram vulcanizates.   The Buna NW vulcanizates show still higher resistance to the development of cracks on wea-

TABLE IVa

COMPARISON OF PROPERTIES OF THERMOVULCANIZATES AND SULFUR–THIURAM VULCANIZATES (UNAGED VULCANIZATES)

Polymer Compound	Buna S 4		Buna S 4/T		Buna NW	
	I	II	I	II	I	II
Stress[1] at 300% elongation (kg/cm²)	66	69	53	71	88	92
Shore A hardness[1]	62	63	61	63	69	65
Spring constant[2] (kg/cm)	386	238	427	360	524	387

[1] Test temperature + 22° C.
[2] At + 75° C.
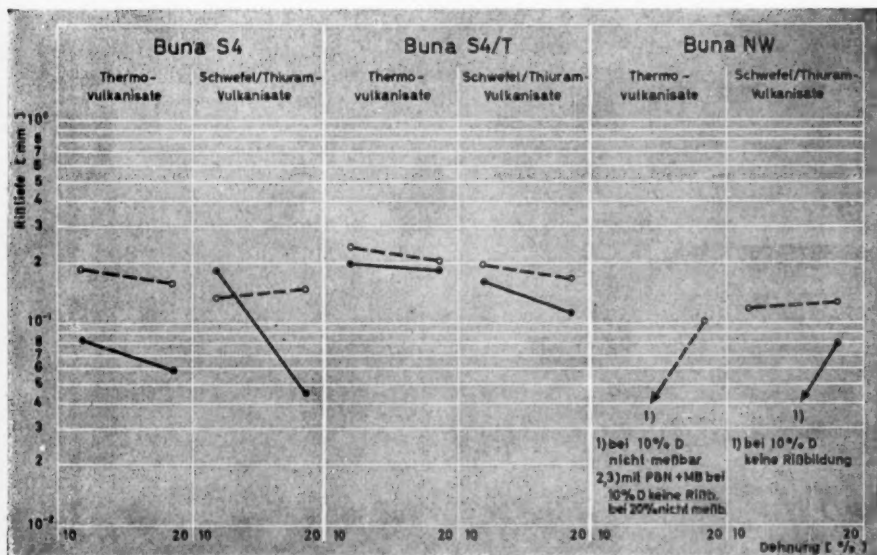
FIG. 4.—Comparison of ozone resistance of thermovulcanizates and sulfur-thiuram vulcanizates. Ordinate: depth of cracks, mm. Abscissa: elongation, %. For Buna NW at 10% elongation 1) no cracks or isolated cracks or cracks less than 10^{-2} mm deep. Also for Buna NW thermovulcanizate 2,3) with PBN + MB at 10% elongation, no cracks, isolated cracks, or cracks less than 10^{-2} mm deep.

ther exposure. The corresponding differences between the two types of vulcanizates are smaller.

The investigation of ozone resistance also reveals differences between the two types of vulcanizates (see Figure 4). The conditions of the ozone resistance test were as follows: 40 parts of ozone in 10^8 parts of air; amount of ozone-air mixture 5 liters/min; ozone generation by mercury vapor lamp; temperature $+22°$ C; measurement of depth of cracks after 4 hours at two different elongations (10% and 20%). The addition of PBN and MB has a beneficial influence on sulfur-thiuram vulcanizates as well as on thermovulcanizates. An especially good result was obtained with Buna NW vulcanizates, the thermovulcanizates in this case again being still better, especially at higher elongation (20%). For thermovulcanizates of Buna S 4 with aging retardants, somewhat better values were found at 10% elongation. At 20% elongation practically no more difference exists, and also for Buna S 4/T vulcanizates the difference is very slight.

The results of aging tests, in part graphically illustrated in the Figures 5a and 5b, give evidence that the thermovulcanizates compare favorably in aging resistance with the excellent aging qualities of the sulfur-thiuram vulcanizates. In the Figure 5a the data for Buna S 4 and Buna S 4/T also indicate that aging retardants in the thermovulcanizates do not produce any improvement in aging characteristics. In general, the aging resistance on thermovulcanizates, as tested in free steam at 125° C and for oxygen exposure, is somewhat better than for sulfur-thiuram vulcanizates. On the other hand the sulfur-thiuram vulcanizates are, in general, somewhat better in Geer aging at 100° C.
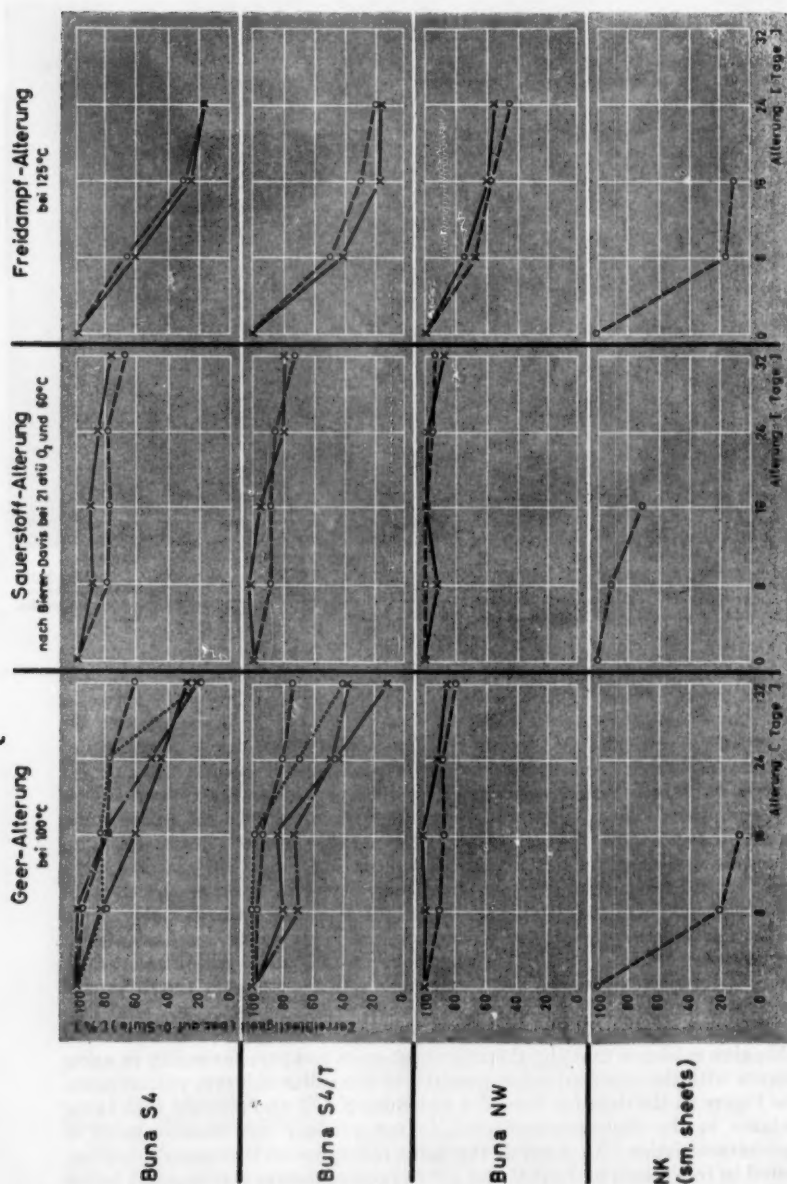
Fig. 5a.—Comparison of aging behavior of some thermovulcanizates and sulfur-thiuram vulcanizates (tensile strength). Designation of curves: x———x Compound I with PBN + MB (thermovulcanizates); x - - - x Compound I without PBN + MB (thermovulcanizates); o - - - - - o Compound II with PBN + MB (sulfur-thiuram vulcanizates); o · · · · · · o Compound II without PBN + MB (sulfur-thiuram vulcanizates). Aging conditions and coordinates are as for Figure 3a.
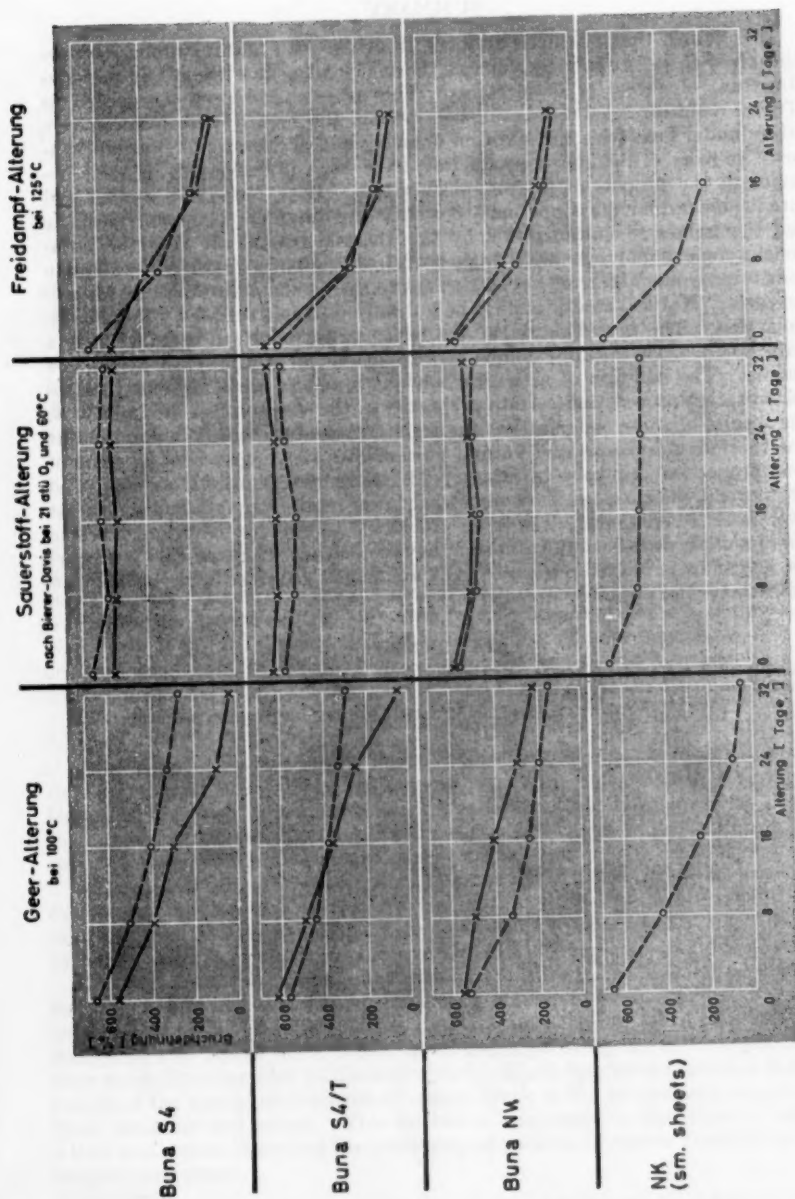
Fig. 5b.—Comparison of aging behavior of some thermovulcanisates and sulfur-thiuram vulcanisates (elongation). Designation of curves: x ——— x Compound I with PBN + MB (thermovulcanisates); o – – – – – o Compound II with PBN + MB (sulfur-thiuram vulcanisates). Aging conditions and coordinates are as for Figure 3b.

SUMMARY

It is shown that synthetic rubbers, in contrast to natural rubber, can be vulcanized to soft rubber by a simple thermal treatment without any previous admixture of sulfur or accelerators. This process has been designated as "Thermovulcanization" to distinguish it from the regular vulcanization procedure under heat with the addition of sulfur and accelerators. Various synthetic rubbers of Schkopau production have been investigated for their behavior in the process of thermovulcanization. Both butadiene-styrene and butadiene-acrylonitrile copolymers as well as the butadiene block polymerizate lend themselves to vulcanization by this thermal treatment. For the butadiene-styrene copolymer with higher styrene content, thermovulcanization leads to products which are not equivalent to the regular sulfur-accelerator vulcanizates. Natural rubber cannot be vulcanized to soft rubber by thermovulcanization. The investigation of the effect of temperature revealed that a temperature of 195° C, for example, was applicable for all the synthetic rubbers studied. The addition of active carbon was found to accelerate the thermovulcanization process and certain properties of the vulcanizates are improved. The results of some comparative studies are presented, and it is pointed out that thermovulcanizates and normal vulcanizates show agreement in some of their properties and vary in others. The thermovulcanizates, as compared with normal vulcanizates, show somewhat lower tensile strength and somewhat lower fatigue resistance. Also their resistance to swelling is lower. On the other hand they are better in abrasion, have somewhat improved elastic properties, and show improved resistance to aging including surface aging phenomena under static and dynamic stress.

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IMPROVING THE CARBON–RUBBER BOND *

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Late in the Eighteenth Century, Immanuel Kant laid a foundation for his philosophy by stating, "We perceive things in space and time because of the nature of our senses."

The approach to the problem of carbon black reinforcement of rubber has been in the same sequence. Emphasis has rightly been placed on the spatial disposition or dispersion of carbon black in rubber as a prime factor for the effective use of carbon black. The present paper has to do with the second of Kant's elements of perception, viz., that of time.

SPATIAL DISPOSITION

In 1820, Thomas Hancock discovered that he could take scraps or cuttings of India rubber and masticate them into coherent masses. From these he could cut sheets or blocks just as readily as from the original imported pieces of rubber. He no longer had to select suitable sizes and shapes from the imported crude to make his cut rubber. He soon found that for even the small masses of one pound which he kneaded in his nail studded cylinder masticator, an inordinate amount of power was required, and he had to put two men on the handle of the machine.

"Mill" mixing of dry colorants and in turn of reinforcing pigments soon followed.

After Hancock's basic discovery of the plastic working and cohesion of rubber, progress in this field has been primarily in the direction of building bigger and stronger machines requiring ever-increasing horsepower to drive them, with ever-increasing damage to both the rubber and the carbon black, as well as to some of the other compounding ingredients.

After 1910, when the impingement carbon blacks were found to have an exceptional toughening action on rubber, most of the work on pigment dispersion was done on carbon black. If carbon black could be dispersed in rubber by a new machine or procedure, then other pigments generally could be also.

In 1920, Wiegand[1] pointed out the role of fineness in the pigment reinforcement of rubber, and this observation served further to focus attention on dispersion. In 1929, Twiss[2] stated the problem rather neatly when he said that zinc oxide and carbon black should be so dispersed in rubber as to reestablish their smokelike character within the rubber. Much discussion ensued as to the nature of the spatial distribution of carbon black in the rubber with regard to ideal, optimum and actual. This discussion was based on the rubber's being a true continuous phase and the possibility of packing in carbon black in tetrahedral arrangement.

To explain the comparatively low optimum loadings of carbon black in rubber, Wiegand[3] in 1936 proposed the discrete rubber theory. He proposed a concept in which rubber rather than carbon black was essentially the inside phase. Striving for Twiss's ideal, Gerke[4] and his associates were granted a patent on a method of obtaining a particulate or smokelike dispersion of carbon black in rubber. They used electrical resistivity of the mix as their criterion of dispersion.

Based on electrical resistivity measurements and on examination of microtome sections of cured tread stocks with the electron microscope, for example, much thought has been given to the significance of the flocculated appearance of carbon black in rubber. Except for Gerke's description of his product, this type of dispersion seems to be the actual and possibly the optimum spatial arrangement for strength with resilience, provided it is reached by the right path. The idea has been pretty well abandoned that carbon black flocculates by carbon black particle-to-particle attractive forces. Both Parkinson[5] and the present author[6] are agreed that the force which brings the carbon black particles into contact during vulcanization lies in the rubber molecular chain, and that during processing prior to vulcanization a good approximation to a smokelike dispersion should be reached.

HIGH H. P. BANBURY MIXING

Because of the very nature of the equipment used and the fact that rubber, whether natural or synthetic, is most generally mixed in the dry, bulk form, the preferred method to attain this "smokelike" dispersion of black in rubber is to mill the carbon black with an elastomer of high viscosity.

Dry mixing seems to have been pushed about as far as it can go, however, both from the point of power input and type of machine, whether the latter be roll mill, Banbury mixer, extrusion-type mixer, pelletizer, etc. In fact it would seem that this approach is not only reaching the zone of "diminishing returns", but may be actually more harmful than beneficial with regard to dispersion and properties of the final vulcanizate.

In this connection, consider, if you will, what goes on in modern, high-speed, high-pressure Banbury mixer during the rubber compounding operation. Today's cost competition calls for shorter and shorter Banbury cycles and therefore tremendous power input.

Let us follow such a Banbury mixing cycle: Styrene-butadiene rubber (LTP, e.g.) is dropped into the mixer; the ram is down just long enough to push the rubber through the throat of the mixer; the ram is brought up; black is added, and, say, some oil. The ram is brought down again. There is a large amount of horsepower exerted on the mix by virtue of the combination of higher-than-normal ram pressures and higher-than-normal rotor speeds. Picture the rubber folding and refolding and engulfing handfuls of carbon black and squeezing it with terrific pressure, compacting it with a force it has never before experienced and then shearing it apart again and pushing it and shearing it into the rubber. It has been supercompacted and then subjected to supershear to undo the damage of the supercompacting.

DEMAND FOR DENSED BLACK

Loose black, once the reinforcing power of carbon black was recognized, wasn't acceptable as the best form for use in rubber goods manufacturing. It was followed, therefore, by densed, heavy compressed, double compressed and,

in due course, dustless or beaded black for bulk handling. Anyone in the carbon black industry can attest to our dilemma on bead quality. The rubber industry customer wants carbon black beads with all of the following qualities at the same time: (a) higher and higher density to provide maximum economy in warehousing; (b) higher and higher bead strength to stand blowing through ducts and around corners without breaking; (c) uniform spheres (no fines or dust); so they will run out of a car and through automatic weighers and into Banbury mixers, like water; (d) beads hard enough for all this type handling and yet soft enough to break down into the original ultramicroscopic particles immediately on contact with the rubber are desired. The beads are always too hard to disperse or too soft to handle, according to the compounder.

IMPROVEMENTS SUGGESTED

The whole business of present-day compounding and mixing seems to be at cross-purposes and not only with regard to the carbon black. The rubber itself is coagulated, dried, pressed into sheets or baled without sheeting, and then plasticized and milled to expose ever fresh surface to the compounding ingredients. Every plant superintendent from Thomas Hancock on has been conscious of the power cost of these operations.

Dissatisfaction with this state of affairs is not new. As early as 1925, Wiegand[7], in describing "The Rubber Compound of the Future," stated:

"In general this will be one emancipated from all breaking-down influences and endowed with all of the setting-up factors. It may be mixed in latex form with a reinforcing pigment completely and uniformly dispersed in tetrahedral piling; a pigment the surface energy of which will be sufficient to prevent any volume increase at any strain."

In the discussion following the formal presentation he stated further:

"I have flowed gas black into the mixing, with carbon tetrachloride and benzol in equal quantities, and have increased the resultant tensile properties by 25 per cent. In my judgment, solvent compounding is thoroughly worth while thinking about."

Again in 1927, Wiegand[8] went still further when he said:

"The present brutal methods of driving carbon black into rubber must be replaced . . . we should all of us welcome . . . an energetic attack upon the problem of making available the enormous surface energy of the carbon black phase without the existing disruption and degeneration of its rubber matrix."

The idea of flowing gas black into a colloidal matrix with the help of a solvent as a disappearing emolient has a much earlier background. The ancient Chinese[9], in preparing their incomparable inksticks, swelled the binding matrix comprising cowhide glue with water and heat to assist in slipping the carbon black into the glue prior to dispersing it in the matrix by shear via pounding in mortars and on anvils.

These expedients have, however, found little or no practical adoption in the rubber industry.

CARBON-RUBBER AFFINITY

In addition to the recognised roles of fineness and dispersion of pigments used for reinforcing rubber there is still another aspect to the problem, viz., the

question of something specific or unique in the mutual attraction of carbon and rubber.   In this area there is far from unanimity of opinion as to the cause of this affinity between the two, except possibly that both are organophilic.

Non-carbon pigments have been made of a fineness exceeding that of commercial tread-type carbon blacks.   In the laboratory and in some specialized applications and properties these are useful, but for the toughening of tire tread rubber to withstand high-speed travel, overloading, rough roads, rapid acceleration or deceleration, carbon black is still unique in combining resilience with toughness to an equalled degree.

Many colloids have been added via latex combinations as well, e.g., resins[10], lignins[11], etc., with some success, but again not for tough high-speed tire service. Today we accept the increase in tensile strength of the styrene-butadiene copolymer from a few hundred psi to 3000 to 4000 psi as commonplace, but to Bostrom and Lange[12] it was so specific that they called it the carbon effect. Further support for this view was developed by Columbian Carbon Co.[13]; to get good snappy cures without the penalty of falling tensile requires 350 to 400 acres of carbon surface per 100 pounds of SBR.

The work of Fielding[14] on bound Hevea rubber also supported the idea that there was something unique about carbon black and its affinity for natural rubber.   When we tried to apply the same test to the styrene-butadiene copolymers, the problem became more difficult.   It was not possible to say whether the benzene insoluble residue was carbon bound rubber alone or a mixture of bound rubber and rubber gel.   The term "carbon-rubber gel complex" [or carbon gel[15,16] for short] was adopted to cover both effects.

The discovery of the positive temperature coefficient of the carbon gel effect[15-17], the resultant need of mixing temperature control, and the translation of this into significant road wear enhancement seem to add weight to Bostrom and Lange's original description of the phenomenon as a carbon effect. Whether this effect is chemical or physical[18], or both, is a question outside the present discussion.   The fact remains that there is a definite affinity between these two colloids, which then leads to the question: Why not handle them as colloids or, more precisely, in aqueous suspensions?   This is the point where the element of *time* enters.

THE LATEX APPROACH

It is only logical that these two colloids should be brought together and allowed to exercise their affinity for each other at the optimum point in their respective life histories, in other words, as dispersions in water.   This idea is by no means new.   Even before the discovery of vulcanization Thomas Hancock[19] was granted a patent on August 5, 1830, on "Ornaments, etc., by Liquid." In that patent he states:

"The principal ingredient used in the improvements for which the patent is granted is liquid caoutchouc, which is obtained from South America, the East Indies, and other places, and when dried forms the substance called India rubber. . . ."

Further on, in discussing the addition of fibrous or other ingredients to his liquid caoutchouc, he states:

"The colouring substances, when solid, must first be ground very fine in water, and the whole composition well stirred and mixed together; but no more of the colouring matter must be used than is necessary to give the colour required."
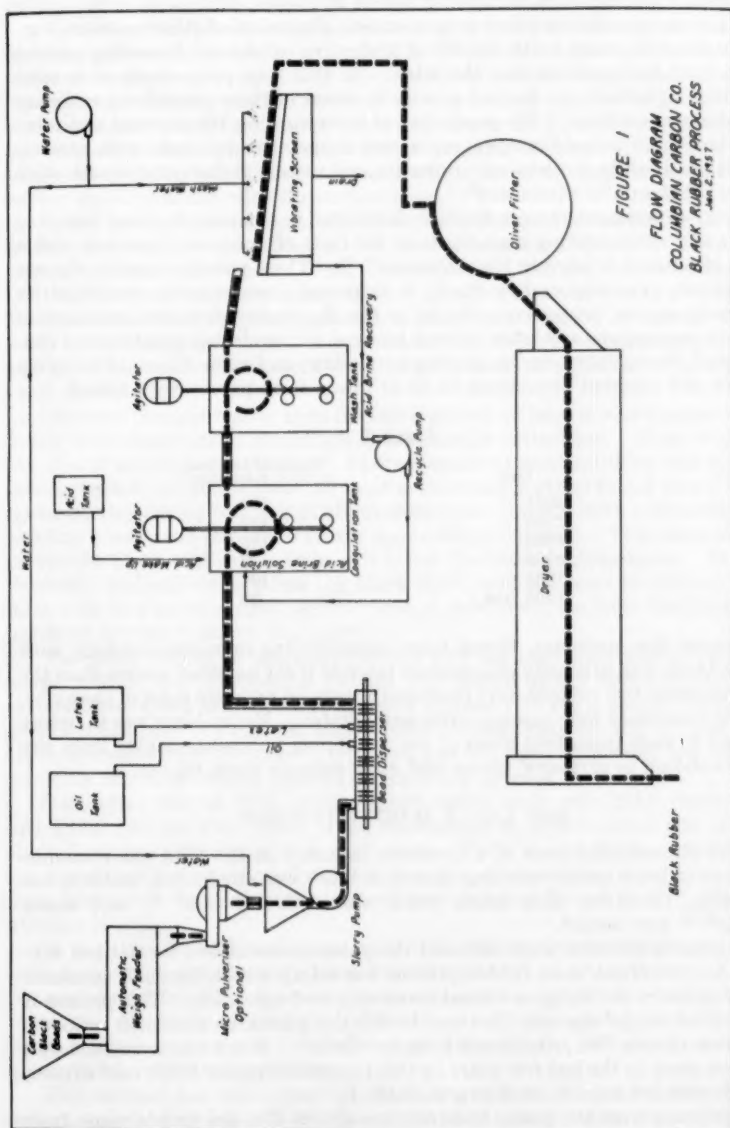
FIG. 1.—Flow diagram of Columbian Carbon Co. latex masterbatching process. Intimate mixing of the carbon black and the rubber latex takes place in cylindrical mixing device just before coagulating tank.

A century later Twiss[2], in the same paper in which he described the ideal of a smokelike dispersion of reinforcing agents in rubber, said:

"It is also possible to effect very complete dispersion of other powders, e.g., carbon black in water (with the aid of protective colloids or dispersing agents) before introducing them into the latex. In this way proportions of a compounding ingredient can be used greatly in excess of those possible by ordinary dry mixing operations. The possibility of incorporating 100 per cent and more of carbon black in rubber opens up a new range of compounds with possible attractions both in mechanical properties and price. Subsequent mastication can be substantially eliminated[20]."

Many experimenters were similarly interested in compounding and handling rubber and compounding ingredients in the form of aqueous dispersion, and a group of patents is listed in the references[21–36]. These patents describe the use of pigment, generally carbon black, in dispersed form suitably stabilized by dispersing agents, protective colloids, or the like; spray drying of mixtures of pigment suspensions and latex; carbon black as a coagulating agent for the concentrated Hevea latex during stirring or mixing; and even alternate spraying of latex and pigment dispersions on to or into a form previously warmed.

TABLE I

Year	Thousand long tons of black masterbatch
1951	124
1952	132
1953	118
1954	77
1955	101
1956 (est.)	99

Despite this optimism, Hevea latex compounding or masterbatching with carbon black was primarily of academic interest if for no other reason than the fact that these two colloids were produced chiefly on opposite sides of the globe, and the economics were consequently unfavorable. Hevea latex was therefore confined to such important areas of use as dipping processes ranging from tire cord insulation to surgeons' gloves and more recently foam rubber.

SBR LATEX MASTERBATCHES

With the establishment of a synthetic industry in the USA the economic handicap of latex masterbatching of carbon black was eliminated, and it is not surprising, therefore, that much work was done on this[37–41], and many patents[42–56] were issued.

In general this new work followed the pattern established for natural rubber. A commercial black rubber process was set up within the SBR synthetic rubber industry during government ownership and operation. This process is summarized by Adams and Howland in Whitby's book on synthetic rubber[57]. It follows closely the principles set up by Twiss[2]. Much black masterbatch has been made in the last few years by this process in regular SBR, cold rubber, and oil-extended rubber, as shown in Table I.

Experience over the years, however, has shown that tire treads made from this type of carbon black masterbatch or black rubber are deficient in wear on the road by something of the order of 5 to 10% when compared with dry mixed (i.e., Banbury) treads of the same composition. This deficiency of car-

bon black masterbatches, despite the convenience of their use, may explain the fall-off in demand for this type of black rubber, as indicated in Table I.

The Columbian process.—A reexamination of the SBR latex black master-batching process apparently was needed. Whenever aqueous dispersions of black are made for sale, as such, it is necessary to add dispersing agents, peptizing agents, protective colloids, or combinations of these. It is well known that carbon black irreversibly adsorbs dispersing agents used for the preparation of aqueous dispersions. In all probability the organophilic end of the dispersing agent remains after coagulation and preempts or blocks off the sites at which the rubber could crosslink with the carbon black.

In dry mixing none of these additives, with the possible exception of fatty acid[58], ever enhanced the rubber-carbon bond as measured by wear. Then why use any of these additives in a black latex process? The problem is to disperse the black in water and keep it dispersed. Grinding in a wet paste, we know to be impractical from long and sometimes costly experience. It seemed worth while to try to disperse the black by some form of violently turbulent hydraulic action. This method was worked out, but as soon as agitation stopped, the black settled out.

The next thought was to keep the black stirred up once it was dispersed and to stir in the latex under conditions of comparable turbulence. Here then was the idea of a continuous process. Various means of accomplishing this type of mixing were tried, and to date the most satisfactory method found uses a high-speed stirring device rotating at about 4000 rpm equipped with a succession of rotating blades and stators to create maximum turbulence. This method disperses the black with water only. It keeps the black in suspension. It continuously and uniformly mixes the black slurry and the latex to a blend, uniform even in a micro range. A flow sheet of the Columbian latex black master-batching process is shown in Figure 1.

The great affinity of black and rubber and the high time rate of reaction between these two hydrophobic colloids were shown by the discovery that the carbon black acted as the creaming agent necessary to get a porous crumb for good washing and drying. So rapid is the reaction between the colloids that the interval between the onset of creaming and full acid coagulation has become probably the most critical element of the whole process.

Columbian process SBR black masterbatches made with HAF (Statex R) and ISAF (Statex 125) black, when road-tested in experimental tire treads, showed marked improvement in road wear. These stocks, when compared in tire treads with conventionally mixed identical stocks of the same base polymer, have given improvements in road wear ranging from 6 to 30% with an average of 15%.

It was also found possible to start with high-molecular-weight polymer latex and made black masterbatches with 25 or 37.5% oil extension on the rubber and containing 50% of carbon on the extended polymer (oil-black masterbatches). Generally speaking, it is desirable, when making a regular LTP-SBR black masterbatch, to add the major part of the normal processing oil to the masterbatch in the same process.

This method has the advantage of making a bale of black rubber that is soft enough to drop into the Banbury for further compounding without risk of breaking the mixer, and it eliminates the tedious job of adding oil to a master-batch of black and rubber alone as was the case heretofore. Also, when most of the oil is masterbatched, the take-up of the remainder of the processing oil of

the compounder's choice at a later stage in the mixing is greatly accelerated when working with the Columbian process black masterbatch. A typical black rubber comprises: rubber, 100; black, 50 to 55; oil, 8 to 10.

This process does not force the black into the latex droplet, but the process does distribute the latex droplets and the black particles to a hitherto unattained degree so that the final dispersion and bonding of the black in the masticated rubber can begin the instant the batch starts around the Banbury. There is no dry black to be compressed and thereby rendered difficult to disperse. A Banbury or extrusion run is still necessary not only to effect the penetration of the black into the rubber, but to generate enough heat to tighten the bond between carbon and rubber in the carbon gel complex.

In general the Columbian Carbon process[59-60] makes possible: (a) lower Mooney viscosity compounds; (b) much better dispersion of black in the rubber; (c) better hysteresis properties of the vulcanizate because of the better dispersion of the carbon black; and (d) an average of 15% better road wear with SBR treads.

SUMMARY AND CONCLUSIONS

Dry mixing involves compacting latex into solid rubber and then tearing it down to make a place for the carbon black. Likewise it involves compacting the carbon both before and after it enters the Banbury and then tearing it apart to develop its full surface. Such operations involve the application of enormous compacting and shearing forces that do neither colloid any good.

By recognizing the *time* element the two colloids are brought together when they both are in a dispersed phase and therefore free to act as colloids; and by taking advantage of the *time* rate of this reaction the process effects the best spatial distribution of black in rubber so far attained. Nothing is added to interfere with the normal affinity of these two colloids. A better distributed and stronger bond results, as is evidenced by substantially enhanced road wear in tires made from such rubber.

ACKNOWLEDGMENT

This process would not have reached success without the enthusiastic assistance of the author's associates, particularly George Heller and J. W. White, of Columbian Carbon Co.'s Hancock Development Laboratory. Sincere thanks are also due to the various polymer companies who made latex available and to the various tire companies who cooperated in the evaluation of the process and who offered encouragement along the way.

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HYDROGENATION OF BUTADIENE RUBBER *

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The study of the chemical structure of butadiene polymers, their chemical reactions and the properties of the products of their transformation reveals a connection between their chemical structure and certain chemical, physical and physical-mechanical properties.   The effect of some factors (the nature of the alkali metal, the temperature and the method of polymerization) on the structure of the butadiene polymer was established by ozonolysis: namely, their effect on the relative proportion of 1,4 and 1,2-butadiene units[1].   It was determined that an increase in the number of 1,4-butadiene units in the rubber has a favorable effect on its technical properties.

In this study the results of an investigation of the process of hydrogenation of a synthetic butadiene rubber are presented.

Most of the existing studies of rubber hydrogenation deal with natural rubber and were designed to determine its structure[2].   Rubber has been hydrogenated on metallic catalysts at various temperatures "en masse" and in solutions of methylcyclohexane, hexahydrotoluene, and ethyl ether.   Hydrorubbers of various molecular weights were obtained, depending on the conditions of hydrogenation.   Hydrorubbers prepared at 270° always had a lower molecular weight than those prepared at 100° and below, and, as a rule, had no elastic properties.   It was later shown that this phenomenon is due to the destruction of rubber molecules at high temperatures[3].   When rubber was hydrogenated in dilute solution at 50–100° the product had a molecular weight[4] of 70,000–80,000.

Previous studies of the properties of hydrogenated rubber, and, in particular, its viscosity, specific weight and index of refraction, have established that in most cases hydrogenated rubber contains products of destruction and cyclization.   In the absence of destruction of the rubber during hydrogenation, the viscosity of solutions of natural rubber is constant and the index of refraction falls.   In the case of cyclization, the index of refraction of hydrogenated natural rubber increases above its original value.   After the completion of this study an article was made available to us in which new rubberlike products of the hydrogenation of polybutadiene emulsion, called "hydropoles" which possess a number of valuable properties, were described[5].

The purpose of this work was: (1) to explain the possibility of selective hydrogenation of the double bonds of butadiene rubber and (2) to determine the relation between the number and the nature of the double bonds in the molecules of rubber and some properties of the latter.   It is known that butadiene rubber contains ethylene bonds of various degrees of substitution, both single derivatives and double derivatives.   On the basis of the work of Lebedev[6], one would expect that the curve of the rate of hydrogenation of butadiene rubber would have a break and that the number of double bonds of various degrees of

substitution could be calculated from this curve. Highly soluble butadiene rubber containing 56.6% of external double bonds was chosen for the present study.

EXPERIMENTAL PART

PURIFICATION OF THE RUBBER, PREPARATION OF CATALYSTS AND METHOD OF HYDROGENATION OF RUBBER SOLUTIONS

Butadiene rubber containing 2% Neozone-D was first purified by precipitating a benzene solution three times with ethyl alcohol; the rubber was then dried to constant weight at 30–35° and residual pressure of 2–3 mm. The rubber was purified and dried in an atmosphere of pure nitrogen[7]. The alcohol and benzene were carefully purified. The benzene used did not contain thiophene. The rubber solutions were hydrogenated in the presence of palladium precipitated on calcium carbonate and nickel, platinum black from platinum dioxide, platinized carbon activated with doses of chloroplatinous acid, and Raney nickel.

The catalysts were prepared as follows. Palladium on calcium carbonate was prepared according to Busch[8]. The palladic oxide hydrate was reduced with hydrogen in heptane immediately before the experiment. One gram of the catalyst contained 0.0122 gram of palladium. The palladium on newly reduced nickel was prepared according to Ginzberg[9]. The newly reduced nickel was obtained by reducing nickel oxide at 280–330° in an atmosphere of electrolytic hydrogen. A dry catalyst was used for hydrogenation. One gram of the catalyst contained 0.0377 gram of palladium. Platinum black from platinum dioxide was prepared according to Adams[10]. The platinum dioxide obtained was reduced with hydrogen in alcohol immediately before the experiment. One gram of platinum dioxide contained 0.795 gram of platinum. Platinized carbon activated with doses of chloroplatinous acid was prepared according to Zelinskii[11]. The platinized carbon was activated by chloroplatinous acid immediately before the experiment. One gram of platinized carbon contained 0.0767 gram of platinum. The Raney nickel was prepared according to Adkins' method[12].

The activity of each of the catalysts named and the suitability of the solvent were tested on allyl alcohol and eugenol, which had the following characteristics:

Allyl alcohol: boiling point 95.5–96°, n_D^{20} 1.4125; eugenol: boiling point 110.5–111° (3 mm), n_D^{20} 1.5408.

The rubber solutions were hydrogenated at atmospheric pressure in Lebedev's apparatus[13] in a glass flask of 500 ml capacity at 20 ± 0.2°. Saturated hydrocarbons (heptane and hexane) were used as solvents for the rubber. The concentration of the hydrogenated solution did not exceed 0.8%. Hydrogen was obtained by electrolysis of a 30% solution of caustic soda. The absorbed hydrogen was calculated every 0.5 minute, with an accuracy of ±0.25 ml.

The hydrocarbons used as rubber solvents had the following characteristics:

Heptane: boiling point 98.3°, n_D^{20} 1.3879, d_4^{20} 0.6839, content of saturated hydrocarbons, sulfur and octane number 0.0; hexane: boiling point 68.8°, n_D^{20} 1.3758, d_4^{20} 0.6596, bromine number 0.1.

EXPLANATION OF THE INFLUENCE OF SOME FACTORS ON THE RATE OF HYDROGENATION OF RUBBER SOLUTIONS

In order to insure the most favorable conditions for rubber hydrogenation, the effect of the intensity of agitation, the quantity of catalyst present, and the

concentration of the rubber solution (with constant proportions of rubber and catalyst) on the rate of hydrogenation of a rubber solution was studied.   The volume of the hydrogenated solution was 200 ml.   The results of a study using palladium on calcium carbonate are shown in Figures 1–3.
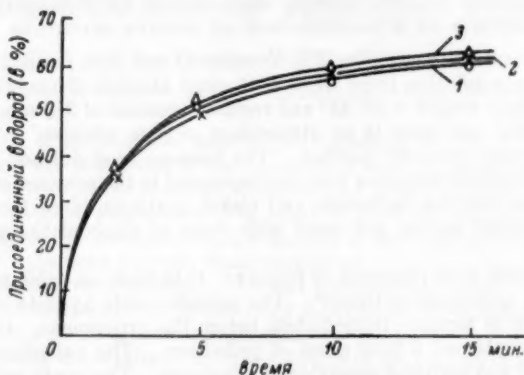
FIG. 1.—Effect of intensity of agitation on the degree of hydrogenation of butadiene rubber on palladium on calcium carbonate.   Intensity of agitation (oscillations per minute): 1—240; 2—350; 3—450.

It is seen from the data presented that the rate of hydrogenation of rubber solutions is independent of the intensity of agitation (Figure 1) within the limits of 240–450 vibrations per minute.   The quantity of catalyst present has a decisive effect on the rate of hydrogenation (Figure 2), since the rate increases noticeably the catalyst content is increased 4 and 8 times over the original amount and, finally, the rate of hydrogenation is practically independent of the
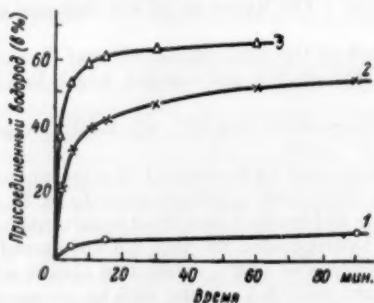
FIG. 2.—Effect of amount of catalyst (palladium on calcium carbonate) on the degree of hydrogenation of the rubber solution.   1—2 g; 2—8 g; 3—16 g.

concentration of the solution within the limits 0.2–0.8% when the proportions of rubber and catalyst are kept at 1:10 and 1:20 (Figure 3).   These results (Figures 2 and 3) show that in order to insure thorough hydrogenation in rubber solutions of concentration 0.2–0.8% it is necessary to use a quantity of palladium on calcium carbonate which will give a ratio of at least 1:20 between the rubber and the catalyst.

It is noteworthy that the nature of the curve of the rate of hydrogenation of rubber in the presence of palladium on calcium carbonate is the same in all cases, regardless of the conditions of hydrogenation; the curve of the rate of hydrogenation of rubber on two different palladium catalysts are shown in Figure 4; three times as much palladium was present in the second case (Curve 2) as in the first (Curve 1).
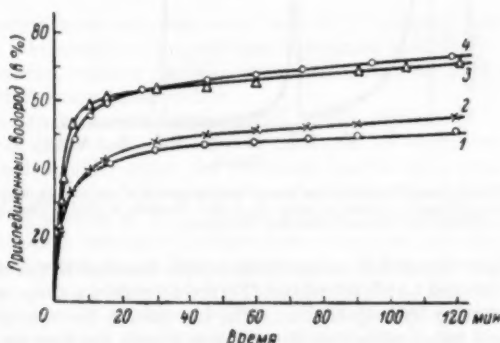
Fig. 3.—Effect of concentration of rubber solution on degree of hydrogenation with constant proportions of rubber and catalyst: 1:10 (1,2) and 1:20 (3,4). (The catalyst was palladium on calcium carbonate.) Concentration of solution in volume per cent: 1—0.8, 2 and 3—0.4.

The sharp decline in the curve of the rate of hydrogenation of rubber might be due to the obstacles to hydrogenation of the double bonds in partially hydrogenated rubber and to a decrease in the activity of the catalyst during hydrogenation. In order to explain the causes of the sharp drop in the curve of the rate of rubber hydrogenation, the effect of new portions of catalyst and rubber on the rate of hydrogenation in the presence of palladium on calcium
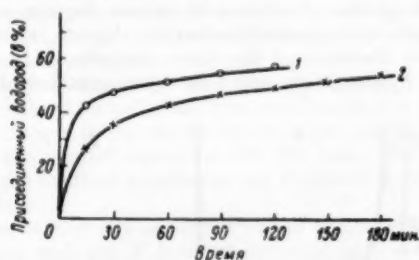
Fig. 4.—Hydrogenation of 0.4% rubber solution with palladium on calcium carbonate (1) and palladium on nickel (2) with a ratio of rubber to catalyst of 1:10. The abscissa represents time in minutes; the ordinate the hydrogen absorbed in per cent.

carbonate was studied. To depict the results of hydrogenation graphically we plotted the time (in minutes) on the abscissa and the quantity of hydrogen absorbed (in milliliters) in separate intervals of time on the ordinate. The results are shown in Figures 5 and 6.

The sharp increase in the rate of hydrogenation when the newly reduced catalyst is used when compared with that when the hydrogenation process was
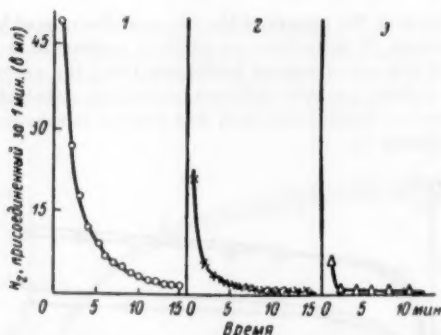
Fig. 5.—Effect of new doses of catalyst on rate of hydrogenation of the rubber solution (catalyst was palladium on calcium carbonate). Doses of catalyst: 1—1st; 2—2nd; 3—3rd. The abscissa represents time in minutes; the ordinate the hydrogen absorbed (ml/min).

interrupted (Figure 5), as well as the considerable decrease in the rate of hydrogenation of the second batch of rubber (Figure 6), reflect a drop in the activity of the catalyst during hydrogenation. The increase in the rate of hydrogenation of the second batch of rubber in comparison with the first batch, in which the process was interrupted (Figure 6), can be attributed to the obstacles to hydrogenation of the double bonds in the partially hydrogenated rubber.

ISOLATION AND STUDY OF THE HYDROGENATED RUBBER

In view of the decrease in activity of the catalysts studied during hydrogenation, it was impossible to trace the behavior of the double bonds in the rubber from the curves of the rate of hydrogenation.

In order to determine whether selective hydrogenation of the double bonds takes place in rubber, and whether there is any connection between the structure and certain properties of rubbers of various degrees of hydrogenation, rubber solutions were hydrogenated to various degrees, as measured by the amount of hydrogen absorbed on the same catalysts. After the absorption of the quantity of hydrogen necessary for hydrogenation of a given rubber
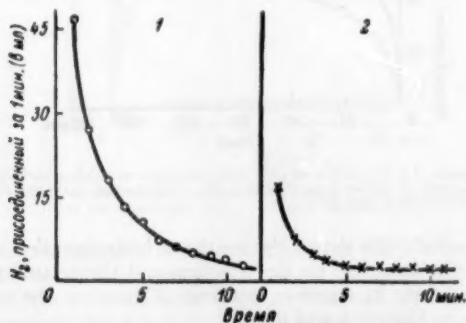
Fig. 6.—Effect of new portions of rubber on the rate of hydrogenation of rubber solution (catalyst was palladium on calcium carbonate). Portions of rubber: 1—1st; 2—2nd. The abscissa represents time in minutes; the ordinate the hydrogen absorbed (ml/min).

sample to the desired degree, nitrogen was bubbled through the flask and the flask was then emptied. In order to separate the catalyst, a solution of products of the hydrogenated rubber was centrifuged at 2500–3000 rpm. Most of the solvent was then eliminated in nitrogen at 30–35° and 100–60 mm pressure. The hydrogenated rubber was precipitated from the remaining solution with purified ethyl alcohol and dried to constant weight at 30–35° and 2–3 mm pressure.

The following measurements were made of the original and the hydrogenated rubber: total unsaturation, content of external and internal double bonds, index of refraction, relative viscosity of benzene solutions (of the same composition), and vitrification temperature.

The total unsaturation was measured with a solution of iodine bromide[14]. The number of outer double bonds was measured by ozonolysis[15]. When rubber is ozonized in chloroform the resulting ozonide is a white gel-like mass which becomes a white loose/porous powder when the solvent is eliminated (15–18 min) in a bath at 20°. When hydrogenated rubber is ozonized the quantity of ozonide insoluble in chloroform decreases with an increase in the degree of hydrogenation, and after elimination of the solvent it is a colorless syrupy mass. The products of decomposition of the ozonides of the original rubber are completely soluble in water. When the ozonides of hydrogenated rubber are decomposed insoluble products are formed; the quantity of these increases with an increase in the degree of hydrogenation.

In order to determine the number of internal double bonds present we compared the curves of the rate of oxidation by benzoyl hydroperoxide of 1-vinyl-cyclohexene-3 and the specimen studied. The method is based on the difference in the rate of oxidation by benzoyl hydroperoxide of the ethylene bond at various degrees of mixing[16].

Benzoyl hydroperoxide recrystallized from alcohol had a temperature of fusion of 103–103.5°. The peroxide was 99.2–99.5% pure, representing 6.56% active oxygen (theoretically 6.61%). The 1-vinyl-cyclohexene-3 (the divinyl dimer) had a temperature of fusion of 65.5-66.2° (100 mm), n_D^{20} 1.4601. The benzoyl hydroperoxide was prepared according to the method of Prikzhaev[17]. The concentration of the peroxide solution obtained was usually about 1 per cent, based on the active oxygen.

The solutions of divinyl dimer and the original and hydrogenated rubber solutions were prepared for oxidation from a calculation of 0.1 N, based on the consumption of halogen in the double bonds of the original rubber, taking the unsaturation of the original rubber as 100 per cent. For this purpose, 0.27 gram of each of the oxidized substances was dissolved in 100 ml of chloroform in a graduated flask.

Oxidation was carried out as follows: equal volumes 0.1 N solution of the oxidized substance and 0.2 N benzoyl hydroperoxide solution were poured into the flask, which was vigorously shaken, and the flask was placed in a thermostat where a temperature of 25° was maintained. At fixed intervals specimens were taken from the flask and titrated with a 0.1 N solution of sodium thiosulfite. From the data thus obtained the proportion of oxidized double bonds was calculated. The divinyl dimer was oxidized under the same conditions.

The index of refraction of the rubber was determined on an Abbé refractometer[18] at 20°. The relative viscosity of 0.08 per cent benzene solutions of rubber was determined in an Ostwald viscometer[19] at 25°. The vitrification temperature was measured on the apparatus of Marei[20].

TABLE I

PROPERTIES OF BUTADIENE RUBBER OF VARIOUS DEGREES OF HYDROGENATION PREPARED WITH VARIOUS CATALYSTS

Catalyst	Per cent of absorbed hydrogen	Unsaturation, %	Per cent of double bonds		Ratio of double bonds 1,2 to 1,4	n_D	Relative viscosity of 0.08% benzene solution	Vitrification temperature °C
			1,2	1,4				
	0	88.2	56.6	37.0	1.53	1.5120	1.247	−60.0
Palladium on nickel	24.6	61.9	—	28.5	—	1.5005	1.228	−65.0
	29.2	56.5	36.2	26.5	1.36	1.4980	1.216	−66.0
	42.0	48.9	—	21.5	—	1.4910	1.203	—
	69.5	19.0	12.7	11.5	1.1	1.4860	1.180	−70.0
Palladium on calcium carbonate	27.2	56.9	38.0	28.0	1.35	1.5000	1.224	−64.0
	54.1	33.3	20.4	19.0	1.07	1.4922	1.197	−66.4
	74.7	11.6	5.6	5.5	1.02	1.4836	1.163	−70.6
	86.3	4.1	—	—	—	1.4081	1.140	−70.5
Platinum black	5.0	85.2	—	—	—	1.5115	—	—
Platinized carbon and chloroplatinous acid	*	35.5	—	—	—	1.4900	—	−67.0
Raney nickel	18.1	—**	50.1	35.5	1.41	—	1.247	−59.5
	42.6	72.7	46.4	34.5	1.35	—	1.29	−59.7
	66.2	—	—	25.5	—	—	—	—

* In the hydrogenation of standard samples of allyl alcohol and eugenol it was shown that with these catalysts it is impossible to calculate the absorbed hydrogen quantitatively.

** The discrepancy between the amount of hydrogen absorbed and the unsaturation of the product obtained is difficult to explain.

PROPERTIES OF DIVINYL RUBBER OF VARIOUS DEGREES OF HYDROGENATION

Results of the study of the properties of butadiene rubber of various degrees of hydrogenation prepared with various catalysts are shown in Table I. It is seen that an increase of the degree of hydrogenation of rubber on palladium on nickel and on palladium on calcium carbonate causes a decrease in the unsaturation and the proportion of double bonds. A decrease in the ratio of external (1,2) to internal (1,4) double bonds in the rubber at a high degree of hydrogenation reflects a certain selectivity in the hydrogenation of the external double bonds.

Since hydrogenation of rubber solutions hardly takes place at all on platinum black, a specimen of hydrogenated rubber was obtained with unsaturation of 35.5 per cent on platinized carbon activated with doses of chloroplatinous acid. The results of measurement of the internal double bonds in the hydrorubber specimen also indicate the absence of complete selectivity in the hydrogenation of the double bonds. A certain preference of the external double bonds for hydrogen was observed on Raney nickel.

Thus the results of measurement of the external and internal double bonds in partially hydrogenated butadiene rubber prepared with various catalysts show that the external double bonds of butadiene rubber are hydrogenated more rapidly than are the internal bonds. Study of the properties of butadiene rubber at various degrees of hydrogenation disclosed a regular decrease in the index of refraction, a decrease in relative viscosity (of an 0.08% benzene solution), and a drop in the vitrification temperature at higher degrees of hydrogenation. The decrease in the index of refraction of rubber with an increase in the degree of hydrogenation indicates the absence of cyclization, since in the opposite case the index of refraction would increase[21]. The drop in the relative viscosity of equal benzene solutions of butadiene rubber with degree of hydrogenation may be due to the destruction and change in shape of the rubber molecules during hydrogenation in connection with changes in the chemical structure of the original rubber.

The vitrification temperature of rubber is closely related to its elasticity. According to the kinetic theory of elasticity[22], the energy of reaction between the rubber chain segments along the chains and between the individual chains depends on the chemical structure of the rubber. Our data on the hydrogenation of butadiene rubber show that the disappearance of the double bonds in the rubber molecule which is related to the conversion of the vinyl groups into ethyl groups and the simultaneous decrease in the double bonds, leads to a decrease in the energy of reaction between the individual chain segments, involving a decrease in the vitrification temperature.

EXPLANATION OF THE CAUSE OF THE DECREASE IN RELATIVE VISCOSITY OF BENZENE SOLUTIONS OF RUBBER DURING HYDROGENATION

In order to explain one of the possible causes of the drop in the relative viscosity of benzene-rubber solutions with the degree of hydrogenation, and specifically oxidative destruction caused by traces of oxygen in the hydrogenated system, rubber was hydrogenated on palladium on calcium carbonate in heptane in the absence of atmospheric oxygen, in both the absence and presence of the antioxidant Neozone-D (phenyl-2-naphthylamine). The solvent was distilled twice in nitrogen; the rubber solution was also loaded from the ampoule

into the flask for hydrogenation in an atmosphere of nitrogen.   Two per cent of Neozone-D was added to purified rubber precipitated from a benzene solution. The properties of the hydrorubbers obtained are shown in Table II.

Table II shows that the drop in the relative viscosity of benzene-rubber solutions during hydrogenation also takes place in the absence of oxidative destruction (in the presence of the antioxidant Neozone-D).   In order to resolve the

TABLE II

PROPERTIES OF HYDROGENATED BUTADIENE RUBBER PREPARED WITH PALLADIUM ON CALCIUM CARBONATE IN THE ABSENCE OF ATMOSPHERIC OXYGEN IN THE PRESENCE AND ABSENCE OF ANTIOXIDANT NEOZONE-D

Hydrogenated rubber	Absorbed hydrogen, %	Unsaturation, %	n_D	Relative viscosity of 0.08% benzene solution
—	0	86.2	1.5121	1.310
Purified	62.2	26.7	1.4905	1.253
Purified 2% Neozone-D	79.8	9.0	1.4838	1.248

question of the destruction of the rubber molecules during hydrogenation, the number and weight average molecular weights of the original and hydrogenated rubber were calculated.   The results are shown in Table III.

The data in Table III show that the weight average molecular weight of butadiene rubber does not change during hydrogenation, indicating the absence of destruction of the high-molecular part of the rubber.   Slight destruction of the low-molecular part of the rubber, which is reflected in the drop in the mean numerical molecular weight of the rubber, cannot be a cause of the lower viscosity of benzene solutions of rubber after hydrogenation.   In order to explain

TABLE III

RESULTS OF MEASUREMENT OF MEAN MOLECULAR WEIGHT OF ORIGINAL AND HYDROGENATED RUBBER PREPARED WITH PALLADIUM ON CALCIUM CARBONATE

Rubber	Unsaturation, %	Relative viscosity of 0.08% benzene solution	Average molecular weight	
			Weight	Number
Original	86.2	1.310	715,000	162,000
Hydrogenated	2.0	1.180	715,000	121,000

the decrease in viscosity of benzene solutions of butadiene rubber during hydrogenation, it is necessary to assume that the disappearance of the double bonds in the butadiene molecule during hydrogenation leads to greater convolution of the molecule and consequently, to a decrease in its range of action in solution; in other words, the decrease in viscosity of benzene solutions of butadiene rubber due to hydrogenation is related to the change in the shape of the molecule.

CONCLUSIONS

1. Solutions of butadiene rubber were hydrogenated at atmospheric pressure and room temperature on the following catalysts: palladium on calcium carbonate; palladium on nickel, platinum black from platinum dioxide, platinized carbon activated with doses of chloroplatinous acid, and Raney nickel.

2. It was established that when butadiene rubber is hydrogenated on these catal sts the activity of the catalyst decreases, evidently owing to its surface being obstructed with products of hydrogenation. It was consequently impossible to study the behavior of the double bonds in butadiene rubber on the basis of the curves of the rate of hydrogenation.

3. Specimens of butadiene rubber were prepared at various degrees of hydrogenation on all these catalysts and the following quantities were measured: total unsaturation, proportion of external and internal double bonds, index of refraction, relative viscosity of 0.08 per cent benzene solutions, and vitrification temperature.

4. It was established that when butadiene rubber is hydrogenated on the catalysts studied the external double bonds of the rubber are hydrogenated more rapidly than are the internal bonds.

5. It was established that an increase in the degree of hydrogenation of butadiene rubber leads to a decrease in the index of refraction, relative viscosity of benzene solutions, and vitrification temperature.

6. The decrease in the index of refraction of rubber during hydrogenation shows the absence of cyclization and can be explained by the disappearance of the double bonds of the rubber molecule.

7. It was shown that the decrease in viscosity of benzene solutions of butadiene rubber with increase in the degree of hydrogenation is due to changes in the shape of the rubber molecule during hydrogenation.

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THE WEAR OF PASSENGER CAR TIRES *

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INTRODUCTION

The wear of pneumatic tires is a complex phenomenon influenced by numerous factors which are often difficult to identify. Road tests, therefore, require a precise analysis of the conditions to which the pneumatic tires are subjected.

Having at hand considerable experimental work and in agreement with recent publications the authors propose certain directives which permit the elimination of disturbing factors, thanks to the use of statistical methods applied to the laying out of an experimental program and to the analysis of the results. The importance of the type of road covered and of the climatological factors is pointed out: ambient temperature, hygrometry, etc., the influence of which one is able to measure. The nature of the tire itself is also considered. But this whole study makes stand out particularly the concept of "severity of the test", expressed as the absolute wear of the reference tire during the test under consideration. This concept of severity which moreover covers the totality of the conditions of experimentation allows the authors to give a new meaning to the laboratory tests on the abrasion machine. Although this correlation still has to be confirmed by numerous tests, it is an interesting attempt which seems to show promise.

The study of the methods for testing the wear of tires in order to determine the resistance to abrasion of experimental mixtures, as well as the execution of such tests has already formed the subject of numerous publications[1,3,4,5,6,14] in the USA as well as in Europe[7,8,9,10] where these methods are now in everyday use. It is known that the results of laboratory tests by means of which one can adjust at will the factors controlling the wear of mixtures are difficultly transposable to the domain of the pneumatic tire. In fact, in the course of a normal use, the latter is subjected to a very large number of influences acting independently or not and making the interpretation of the results difficult.

In over three years the investigations undertaken at the Rubber-Stichting and at the IFC have made possible the realization of about 400 tests both on the normal road and on the track. In analyzing these experimental data one has thus been able to verify the influence of a certain number of factors such as the position of the tire on the vehicle, the ambient temperature, etc., and one can throw light on the factors which dominate the severity of the tests, this severity playing a controlling role in the results of the experiments, and one can observe certain correlations between the various test conditions.

TEST METHODS

All of the authors already cited have stressed the necessity of operating under well defined experimental conditions to obtain reproducible results with good precision.   This idea, coupled with economic considerations, has led to the conception of "typical tests" carried out under as precise conditions as possible.   One can imagine that tests effected on special vehicles, used on different roads, at speeds and loading conditions which are variable, cannot give results which are as precise and as reproducible as tests effected on one or more vehicles specially reserved for this purpose, operating at constant load and speed on the same carefully chosen roads.

Be that as it may, it has been attempted to compare the results on relative wear furnished by the special vehicles with those obtained by series of tests on private cars.   Table I summarizes the observations made in the course of studies on the behavior of different rubber-synthetic resin combinations.   One will note that the wear figures originating from the special vehicles are higher in general than those recorded by means of private cars.   This is certainly due to the "severity" of the tests.   This severity, as we shall see later on, plays an important role in the estimation of the relative values of the mixtures and can be expressed as being the absolute wear observed for the comparison mixture in the course of the test in question.

Notwithstanding the perturbing influence of this severity one notes that the limiting zones of the two types of experiments (written between parentheses under the average result) cover each other to a large extent.   Evidently, in the statements at the left hand side of Table I the influence of all conditions of use is neglected, an influence which it is attempted to eliminate by calculating a median value from a larger number of measurements.   This method is both not precise and expensive[12].   In fact, to arrive sensibly at the same result it was necessary in the first case to use at least ten tests of about 10,000 km each, spread over 12 to 20 months, whereas in the other case 4 precise tests of 2000 km were made, a distance which can easily be covered in a week.   One can, nevertheless, ask oneself, if from the sole point of view of wear, the results obtained in the course of tests of short duration using only a small proportion of the tread (10 to 20 per cent as maximum) are comparable with those of tests of long duration going almost up to the disappearance of the design of the tread.

This fairly controversial subject has been treated in various publications[2,4,5,14].   Comparative tests are now being made, but one has already a certain number of indications[2,3,7,8] according to which the relative resistance to wear of tires does practically not vary during the period of use after neglecting a preliminary period of about 500 km.   It seems that one may be satisfied with relatively brief tests in the course of which the experimental conditions will only be subjected to a minimum number of variations.

Usually, the wear undergone by a pneumatic tire in the course of experimentation is checked either by measuring the losses in depth of the tread indentations[1,2,4,5,7], or by weighing before and after the test[1,2,5,6,8,10].   One has found, in practice, that the two methods are sensibly equivalent[2,11].   One can, therefore, determine in the course of a "typical test" a resistance to wear for a given mixture but it is not possible to deduce with precision the absolute resistance to wear of this mixture.   On the contrary, one can calculate with precision the relative resistance to wear of the mixture for the experimental conditions

TABLE I

CORRELATION BETWEEN THE TESTS ON PRIVATE CARS AND ON SPECIAL CARS FOR A FEW TYPES OF RUBBER–RESIN MIXTURES

Type of rubber used	Private cars				Special cars (road)			
	Type	Total number of tests	Total km covered X1000	Ratio of wear of experimental rubber to comparison rubber		Type	Total number of tests	Total km covered X1000	Ratio of experimental rubber to comparison rubber

Type of rubber used	Type	Total number of tests	Total km covered X1000	Ratio of wear of experimental rubber to comparison rubber	Type	Total number of tests	Total km covered X1000	Ratio of wear of experimental rubber to comparison rubber
R (formaldehyde-resorcinol resin)	4 HP Renault Vedette (Ford) Citroën 11B	18	148	1.57 (from 1.17 to 2.34)	Peugeot 203 U Renault "Frégate"	4	8	2.40 (from 2.14 to 2.68)
A (Aniline-formaldehyde resin)	4 HP Renault Peugeot 203 Simca Aronde Vedette (Ford) Citroën 11 B	13	142	1.15 (from 1.02 to 1.35)	Peugeot 203 U Renault "Frégate"	4	8	1.35 (from 1.18 to 1.55)
M.U. (melamine-urea-formaldehyde resin)	4 HP Renault Citroën 11 B Vedette (Ford)	10	91	1.43 (from 1.35 to 1.59)	Renault "Frégate"	5	10	1.67 (from 1.49 to 1.85)

chosen; this relative resistance is given by the formula

$$U_r = \frac{\text{Wear of the experimental tire}}{\text{Wear of the control tire}}$$

The judicious choice of the form of the "typical test" permits moreover calculating, on the basis of the experimental data, a variation coefficient of the wear after elimination of the perturbing factors. This problem is resolved by the use of statistical methods applied to the determination[2,3,4,6,7] of the experimental program and to the analysis of the results. For all of the tests mentioned in this article, the method described by Stiehler and his collaborators[2,3] has been used. It is briefly as follows.

The four tires to be tested are rotated after each test period in order to occupy the 4 possible positions on the vehicle. The direction of the rotations is determined by the typical 4×4 Latin Square, taking into account the fact that it is preferable—to regularize the wear—to reverse the direction of rotation of the wheels after each driving period.

The wear is measured by weighing the tires before and after each of these periods. To obtain good precision, the wheel equipped with its tire, equilibrated both statically and dynamically is carefully washed to eliminate any trace of mud or dust, then dried to constant weight at 38–40° C in a specially ventilated oven. The weighing is done on the deflated tire by means of a precision balance sensitive to $\frac{1}{5}$ gram. In practice, one is satisfied to determine the weight to $\frac{1}{2}$ gram. When necessary, the data of the weight losses of the treads are changed into volumes, to take into account differences in density which may exist between the different mixtures tested.

In the typical 4×4 Latin Square, at least one of the tires used serves as a control. The wear data are calculated by the geometrical averages method, a method which, theoretically, permits eliminating the particular influence of the period and position factors, as one can verify by examining in more detail the Latin Square described by Stiehler[2,3,11].

If, for example, one calls

a, b, c, and d the relative wears of tires A, B, C, and D experimented with by reference to any tire used for control, and

k, l, m, and n the relative wears for the wheel positions AV G (front left), AV D (front right), AR G (rear left), and AR D (rear right) with respect to any position of reference, and

w, x, y, and z the relative wears for test periods 1, 2, 3, and 4 with respect to any period of reference,

we will obtain the wear values shown in Table II.

One can see that if one calculates the wear ratios among the tires, they are independent of the factors influencing the periods and the positions. For example, we have the following:

$$U_r = \frac{\text{Wear of tire B}}{\text{Wear of tire A}} = \frac{b\sqrt[4]{klmnwxyz}}{a\sqrt[4]{klmnwxyz}} = \frac{b}{a}$$

Evidently the same holds for the periods and for the positions. The methods of statistical calculus permit, in addition, the calculation of the total variation intervening for the whole of this Latin Square, as well as the partial

variations due to the factors: tires, periods and positions.   One can thus find by
difference the residual variation which furnishes an estimate of the error made
in the test, from which one can deduce the limits of trustworthiness to 95 per
cent, between which is located the ratio of wear between an experimental tire
and its reference tire.

For the whole of the experiments this error approximates 10 to 15 per cent,
but the precision of a particular test may vary considerably in one sense or the
other of these values, for it is tied practically to all of the factors capable of
influencing wear (test speed, load, type of route, type of driving, weather condi-
tions, etc).

Finally, let us specify that for the majority of the tests cited in the course of
this article, three types of vehicles have been utilized riding with a load of 300
kg, driver included; they are the following: 1 Peugeot "203" car (utilitarian
400 kg); 2 Renault "Frégate" cars; and 2 Ford "Mainline" cars.

<div align="center">TABLE II</div>

<div align="center">4 × 4 LATIN SQUARE AND CALCULATION OF THE
GEOMETRICAL AVERAGES OF THE WEAR</div>

Periods \ Tires	A	B	C	D	Geometrical average per period
1	akw	blw	cmw	dnw	$w\sqrt[4]{abcdklmn}$
	AVG	AVD	ARG	ARD	
2	alx	bmx	cnx	dkx	$x\sqrt[4]{abcdklmn}$
	AVD	ARG	ARD	AVG	
3	amy	bny	cky	dly	$y\sqrt[4]{abcdklmn}$
	ARG	ARD	AVG	AVD	
4	anz	bkz	elz	dmz	$z\sqrt[4]{abcdklmn}$
	ARD	AVG	AVD	ARG	
Geometrical average per tire	$a\sqrt[4]{klmnwxyz}$	$b\sqrt[4]{klmnwxyz}$	$c\sqrt[4]{klmnwxyz}$	$d\sqrt[4]{klmnwxyz}$	
Position	AV. Gauche	AV. Droit	AR. Gauche	AR. Droit	
Geometrical average per position	$k\sqrt[4]{abcdwxyz}$	$l\sqrt[4]{abcdwxyz}$	$m\sqrt[4]{abcdwxyz}$	$n\sqrt[4]{abcdwxyz}$	

These cars are all equipped with recording equipment making possible the
control of the test speed.

Depending on the case, these vehicles are equipped with 165 × 400, 185 ×
400, 640 × 15 or 670 × 15 tires, inflated to the normal pressures recommended
by the manufacturers for the load and the type of vehicle used.

These cars can be driven on several test circuits, namely:

In Holland:

　Automobile highway The Hague-Utrecht-Amsterdam;
　Eindhoven-Roermond highway;
　Route in the Belgian and Luxemburgian Ardennes (Maastricht, Liège,
　　Spa, St. Vith, Ettelbruck, Mersch, Echternach, Diekirch, St. Vith,
　　Liège, Maastricht).

In France:

　Montlhéry, Dourdan, Ablis, Chartres, Le Mans, La Flèche highway and
　　return;

Nimes, Montpellier, Narbonne, Perpignan and return;
Road circuit of 9180 km of the Linas Montlhéry race track.

Except for the Montlhéry track on which the wear values are extremely
high, the length of travel between 2 measurements of wear varied between 400
and 500 km.

FACTORS AFFECTING WEAR

It is known that the factors which may affect wear are extremely numerous
and often difficult to detect in the course of a normal test as their causes are
often complex.   In order to try to fix the ideas these factors may be broken
down into two large categories:

1—Those which may be determined by the experimenter.
2—Those which escape him and which are due to chance.

This notion of hazardous factor is nevertheless fairly vague for under certain
conditions an uncertain factor may become determinate, or at least its import-
ance may be reduced very much.   For example, rain in the course of a test is
considered as a disturbing factor, independent of the known data of the
experiment; it is possible, however, to avoid it by suspending the test on rainy

TABLE III

INFLUENCE OF THE CONDITION OF THE SUSPENSION ON THE
RELATIVE WEAR BY POSITION OF PNEUMATIC TIRES

Position	Ratio of wear by position	
	Normal	Abnormal
Front left	1.00	1.00
Front right	0.90	0.95
Rear left	0.77	1.21
Rear right	0.63	1.05

days.   One may also attempt a classification of the perturbing effects by order
of importance.   Unfortunately the appreciation of this importance always
remains subjective.

It has been judged preferable, although it is arbitrary, to consider in the
first place the effects which have principally a repercussion on the factors of
"position, period and tire" defined by the typical Latin Square, and to study
the more complex effects later.

Factors influencing wear and depending on the position of the wheels.—The
position of the tire on the vehicle has a very great importance from the point
of view of wear[1,2,5,6,7,8] although it is possible theoretically, as we have seen
above, to eliminate this influence by means of a mathematical artifice.   It is of
interest, nevertheless, to consider the mode of action of the experimental condi-
tions on this factor.   In the first place the mechanical defects of the vehicle
should be mentioned, such as the parallelism of the wheels or the condition of
the suspension.

By way of example, here are a few figures taken from tests on the stretch
Montlhéry-La Flèche with a Renault "Frégate" car (Table III).   The left
front wheel is used for comparison.

The anomaly of relative classification of the different positions has shown an
accidental deterioration of the left rear shock absorber with repercussion on the
right rear position.   It must be mentioned that a careful inspection of the test

data often allows the detection of such a defect even before it becomes perceptible by the driver. Thus, there is in this manner an effective means of verifying certain test conditions.

Thus it has been possible to compare the behavior of three types of vehicles used in the researches (Table IV) on the 9180 km Montlhéry road circuit.

One notes that the front wheels of the Renault and of the "Mainline" Ford wear more than the rear wheels whereas the opposite is true for the Peugeot 203 U.

TABLE IV

RELATIVE CLASSIFICATION OF THE POSITIONS OF THE WHEELS
FOR THREE TYPES OF VEHICLES

Position	Peugeot 203	Renault "Frégate"	Ford Mainline
Front left	1.00	1.00	1.00
Front right	0.88	0.89	0.93
Rear left	1.65	0.71	0.42
Rear right	1.24	0.60	0.51

Finally, just like the type of vehicle, the type of test circuit used, by influencing the severity of the tests, may also affect this classification as is shown by the figures in Table V as well as by Figure 1.

This quick review shows up clearly the necessity of operating under conditions which are as definite and as reproducible as possible, in order to obtain results which are comparable from one test to the other. It can be seen also that the passage from one set of experimental conditions to another may bring about a search for correlations between the diverse elements which enter into the determination of the wear.

TABLE V

INFLUENCE OF THE TYPE OF TEST ROUTE ON THE
RELATIVE WEAR BY POSITION

Position	Eindhoven-Roermond	Ardennes
Front left	1.00	1.00
Front right	1.10	1.16
Rear left	1.14	0.70
Rear right	1.00	0.68

Severity in cc/1000 km.

Factors affecting wear in the course of the test periods.—The variations in wear from one test period to another, often originate from causes which are difficult to define. It has been thought that atmospheric factors were at the origin of these perturbations; they escape to a large extent the will of the experimenter who must limit himself to the making of such an observation.

Thanks to the meteorological station of the Linas Montlhéry race track, it has been possible to study, during the various tests, the influence of these diverse factors on the wear of pneumatic tires.

One of the most important factors is made up of atmospheric precipitations; the presence of a coating of wetted soil in all cases brings about a decrease in wear. It has been possible to establish, on the basis of the known experimental data and the comments made by the drivers in the notebook carried in the vehicles, a sort of wear scale as a function of the raininess. One can also calcu-
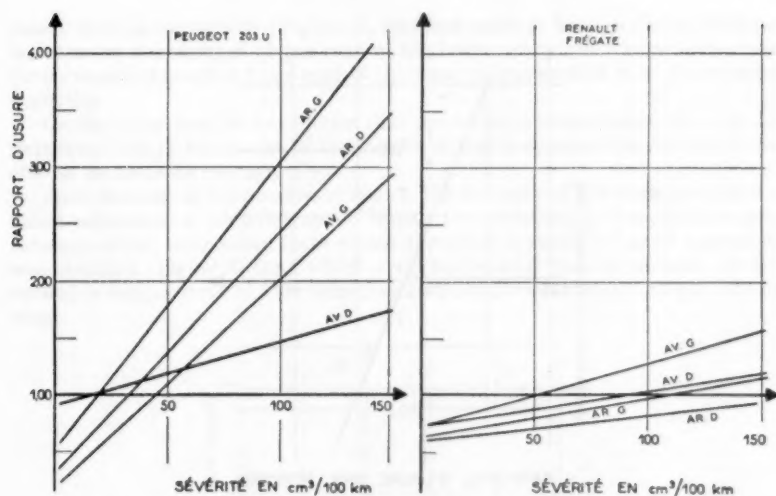
Fig. 1.—Influence of the severity of the tests on the relative wear (ordinate) by position (Montlhéry race track).

late on the basis of the known data of the experiment, an approximate correction factor applicable to the disturbed period. Table VI summarizes some typical data obtained in the course of tests on the Montlhéry road track.

The rain is not the only atmospheric factor which intervenes in the course of the tests with pneumatic tires. It has been thought that the hygrometric

TABLE VI
INFLUENCE OF THE RAIN ON THE WEAR PER PERIOD

Average wear during non-rainy periods (cc/1000 km) (1)	Average wear during rainy periods (cc/1000 km) (2)	Ratio Col. (1) / Col. (2)	Remarks*
209	196	1.07	Brief shower—ground drying rapidly
732	627	1.18	Rains several times in succession—ground drying rapidly—about 10 to 15% of the stretch driven on wet highway
730	308	2.37	Heavy soil drying with difficulty in spots, 35–50% of stretch driven on wet highway
841	196	4.30	Rain during 50% of the distance. Circuit wet during about 70–75% of the test period
138	14	9.80	Practically continuous rain during the entire test period

* Taken from the roadlogs of the drivers.
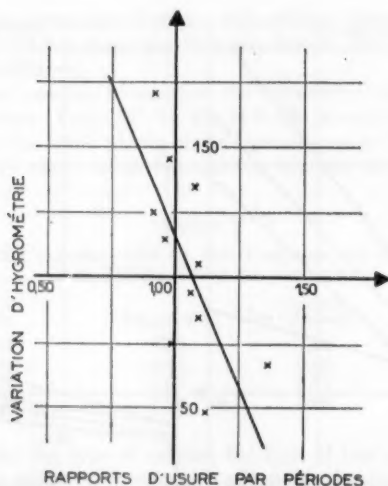
Fig. 2.—Influence of the variations in the hygrometric conditions (ordinate) of the ambient air on the relative wear (abscissa), by periods, of pneumatic tires.   Each point represents the average of about 10 readings.

condition of the ambient air could also have a marked influence on the wear. It was difficult to detect this effect as the diversity of the tests made, as well as the variations of the climatological conditions, made a direct analysis of the phenomenon practically impossible.   However, when plotting the hygrometric variations from one test period to another as a function of the wear ratios be-
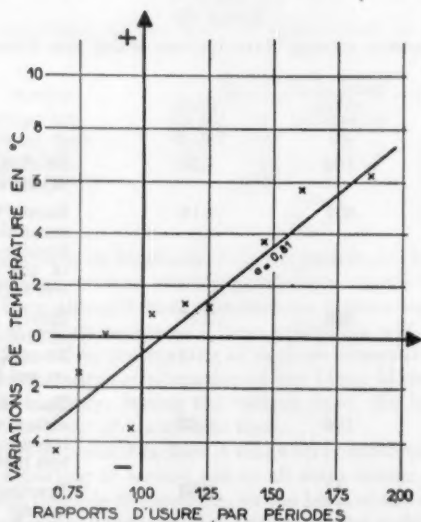
Fig. 3.—Influence of temperature variations of the ambient air on the relative wear by periods (abscissa), Each point is the average of 10 readings.

tween these same periods (Figure 2), one has come to the conclusion that an increase (or decrease) of 10 per cent in the hygrometry could cause a decrease (or increase) of about 3.5 per cent of the wear, a figure which is far from being negligible.

On the other hand it was known that the ambient temperature can play an important role in the course of the tests[2,4,7,9] and it appeared interesting to be able to measure its average effect.

As in the case of the relative humidity, the diversity of the tests prevented a direct estimation of its influence.   Plotting the variations in temperature as a function of the wear ratios from period to period, a straight line of regression was obtained (Figure 3) from which could be deduced that an increase (or decrease) in temperature of 1° C caused an increase (or decrease) of 12 per cent in wear.
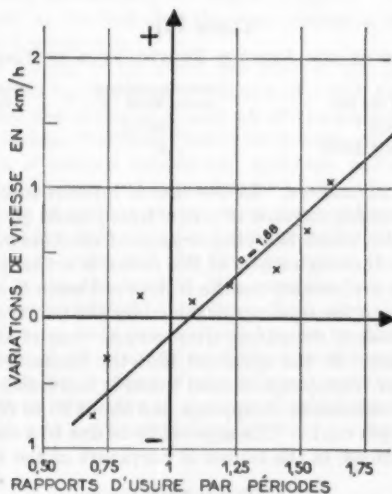
FIG. 4.—Influence of the variations in speed (ordinate) on the relative wear by periods (abscissa).   Each point represents the average of about 10 tests.

This value appeared to be exaggerated and so it was thought that a perturbing effect in the same direction had superposed itself on the temperature effect.   It seemed to have as origin the variations in wear due to the variations in average speeds from one period to the other.

The close examination of the speed records obtained in the course of the experiments has made it possible to establish Figure 4 giving the variations in wear ratios from period to period as a function of the variations in average speeds.

One could, therefore, estimate the slope of the real wear curve as a function of temperature by difference between the calculated slopes of the straight lines of Figures 3 and 4.   This ended up as a variation of the order of 3 per cent/° C.

However, it has been attempted to confirm this figure by trying to measure directly the influence of the temperature on wear.   For this purpose two test series have been carried out, as identical as possible from the point of view of experimental conditions, but by choosing two periods of the year which were

capable of giving respectively a high and a low average temperature.   One can verify from the data given in Table VII, that the average coefficient is 3.3 per cent/degree, a figure which is in good agreement with the result found previously by differentiation of the temperature and speed effects.

Factors affecting pneumatic tire wear directly.—One is once more faced with extremely complex phenomena, in which the frame of the pneumatic tire as well as the type of the tread intervene in various degrees.

For the realization of wear tests on pneumatic tires one of the problems which the experimenter faces is that of knowing if the utilization of recapped tires leads to comparable results with those obtained on new tires.   Let us specify that for the majority of the tests of which mention is made here the term recapping has a special meaning.   In fact, there is generally understood by this term the application of a new tread on a tire which has already been run

Table VII
Influence of the Ambient Temperature on Tire Wear

Date of the test	Average ambient temperature ° C	Average wear in cc/1000 km
July 1955	$+26° 5$	176
February 1956	$-2°$	91

a certain number of kilometers.   In the case of interest to us here, it has to do in reality with the putting in place of a new tread, made up of an experimental mixture, on a new tire which has been uncapped mechanically, i.e., which has never been used.   A thorough study of this factor is actually being carried out, but according to the preliminary results it does not seem that there is a significant difference between the readings obtained by the two types of experiments.

In the case of classical recapping after normal wear of the original tread it is no longer the same.   It was observed that the kilometers accumulated, as well as the number or recappings, tended towards increasing the wear slightly; for example, for two successive recappings and about 20 to 25,000 km of travel, wear increases 4 to 6 per cent.   This appears to be due to a change, in the course of the various operations, of the radius of curvature of the tread[14].

Table VIII
Influence of the Storage Time on the Wear Resistance

	Fresh tires	Stored tires
Wear in cc/1000 km	36.6	34.4

Nevertheless, in order to minimize this parasitic evolution it is preferable to carry out the tests by utilizing tires of the same origin having undergone the same treatment cycles.

Another interesting point to be considered is that of the natural aging of pneumatic tires in storage which may cause changes in the resistance to wear of the tread.

The tests undertaken have put in competition several groups of pneumatic tires freshly recapped by means of natural rubber treads, loaded with 50 per cent of HAF carbon black, and groups of identical tires normally stored in the warehouse for 13 months.   It has been found (Table VIII) as a whole that storage increases the resistance to wear of the mixture by about 5 to 6 per cent.

It must be noted that the results seem to be in disagreement with those published by Stiehler[2] and by Phillips Chemical Co.[13] in which the authors observed

TABLE IX

INFLUENCE OF THE TYPE OF MIXTURE ON WEAR

Mixture with a natural rubber base containing	Wear in cc/10000 km	Wear ratio: experimental rubber to reference rubber
100 chalk	2620	4.18
12.5 resin R	2380	3.80
50 SRF black	1150	1.84
33 resin A	908	1.45
50 MPC black (reference)	627	1.00
50 HAF black	570	0.91
50 SAF black	514	0.82

a decrease of the wear resistance in the course of aging. It is probable that this divergence is caused by the fact that the wear resistance as a function of aging time goes through a maximum.

Among all the factors which affect the wear of the tires, one of the most important is furnished by the type of mixture of which the tread is composed. This point has been the object of almost all of the tests made by the Institut Français and the Rubber Stichting, which have been concentrated particularly on the comparison of natural rubber and synthetic rubber (cold rubber), on the influence of the extension of natural rubber with oils, on the estimation of the respective values of various rubber-resin combinations, on the importance of the quality and of the quantity of the loading materials in the mixtures, etc.

It is not possible to enter into the details of these studies which by themselves alone could make the subject of a separate paper. To illustrate the influence of the type of mixture there have been assembled in Table IX the results observed during tests made at 60 km/hr on the road circuit of the Montlhéry race track, for certain types of loading materials.

However, the relative position of the different mixtures are not unchangeable and may vary as a function of the experimental conditions[5,7,9].

For example the ambient temperature, all other conditions being equal, may
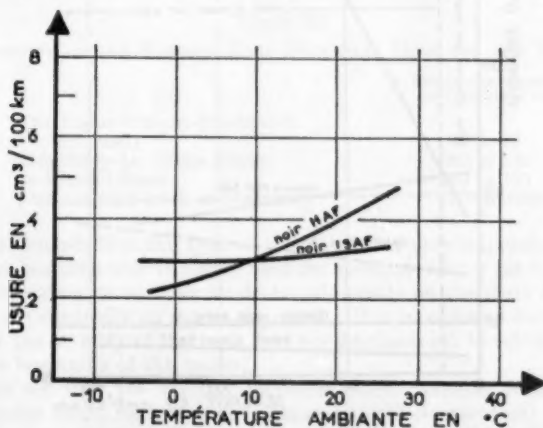
FIG. 5.—Wear (ordinate) as a function of the temperature for mixtures of natural rubber loaded with different carbon blacks.
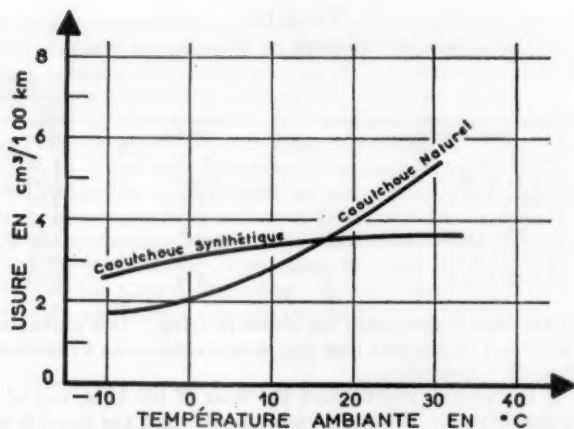
Fig. 6.—Wear (ordinate) as a function of temperature for natural rubber
and synthetic rubber (cold rubber).

change the order of the classifications (Figures 5 and 6), as the course of the
curves shows.

In general, the "severity" of the test (which, let us recall, may be expressed
as the absolute wear of the reference tire during the test under consideration)
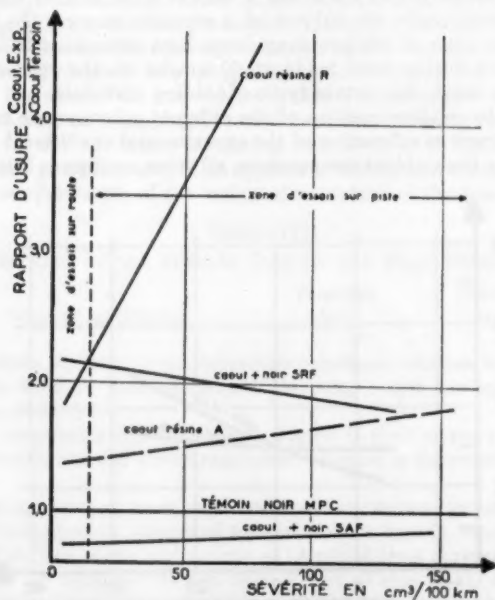
Fig. 7.—Influence of the severity on the wear ratio (ordinate) of various tread mixtures of experi-
mental rubbers to the reference rubber (temoin noir). *Caout resin R* means rubber resin R; *zone d'essais
sur piste* means zone of race track tests; and *caout + SRF noir* means rubber + SRF black.

modifies profoundly the appreciation of the relative values of the various mixtures. Figure 7 (in which for clarity of the figure the experimental points have not been plotted) demonstrates quite well the importance of this factor.

One is thus in the presence of a complex phenomenon as the severity of a test is in fact a function of the totality of the experimental conditions such as, for example, the climatological conditions, the type of driving, the median speed of the test, the type of circuit or of vehicle, etc.

TABLE X

INFLUENCE OF THE DRIVER ON THE SEVERITY OF THE WEAR TESTS

Vehicles	Test course	Average speed, km/hr	Driver no.	Wear in cc per 1000 km
Renault Frègate	9180 km circuit of Montlhéry	60–62	1	1000
			2	1320
	Montlhéry-LaFlèche circuit	80–85	1	77
			2	86
	Ardennes circuit	70–75	1	300
Ford Mainline			2	198
			3	174
			1	—
	Eindhoven-Roermond circuit	80–90	2	33
			3	49

It was interesting to be able to determine the order of magnitude of certain of these factors. Thus one finds in the course of different tests that the driver, and thus the type of driving, has an importance which is not negligible (Table X), even when the different vehicles move as a group, thus at the same average speed.

As we have already seen in the course of the study of the factors affecting the wear, in accordance with the position of the wheels, the type of vehicle intervenes. Thus, one has observed that under identical conditions of use the Peugeot 203 U wore out the tires about 1.4 times less than the Renault "Frégate" and the Ford "Mainline".

TABLE XI

SEVERITY OF THE VARIOUS ROAD STRETCHES USED FOR THE TESTS

Run	Severity expressed in cc/1000 km of run
The Hague-Utrecht-Amsterdam (auto road)	30 to 70
Montlhéry-La Flèche circuit	80 to 120
Ardennes Circuit	180 to 350
9180 km road track at Montlhéry	150 to 2000

It is also known that the type of circuit used is very important. In fact, every driver has been able to realize that the speed of wear of his tires was very different depending on whether he drove principally on the main highways, in the plains or principally on mountain roads. It is in order to be able to vary more easily the severity of the tests that one has been led to select the courses cited at the beginning of this paper.

One can see that the severity increases when changing from an almost straight course (auto highway The Hague-Utrecht-Amsterdam) to a circuit offering numerous turns of high intensity (Montlhéry track). This is due to the fact that the wear increases very sharply with the average turning angle of
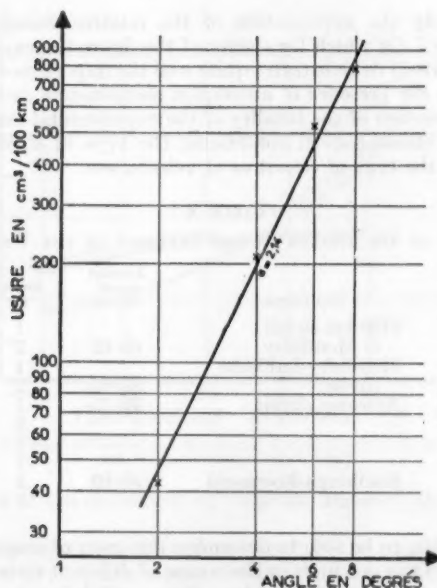
Fig. 8.—Relation of turning angle/wear for natural rubber tires.

TABLE XII

RELATIONSHIP BETWEEN THE WEAR RESULTS OBTAINED ON THE
HIGHWAY AND ON THE TRACK

Vehicle used	Dimension of the tire	Type of natural rubber mixture	Test speed	Wear in cc/1000 km		Wear ratio track road
				Track	Road	
Renault Frégate	185 × 400	HAF black	40	220	42	5.2
			50	450	62	7.3
			60	800	84	9.5
			70	1480	111	13.3
			80	2560	140	18.3
Renault Frégate	165 × 400	HAF black	40	260	40	6.5
			50	480	54	8.3
			60	900	74	9.0
			70	1480	96	15.5
			80	2410	124	19.3
Renault Frégate	165 × 400	MPC black	40	245	36	6.8
			50	400	46	8.7
			60	660	59	11.2
			70	1150	71	16.2
			80	2170	89	24.4
Peugeot 203 U	165 × 400	HAF black	40	70	12	5.8
			50	130	19	6.9
			60	260	27	9.7
			70	620	39	15.9
			80	1960	53	37.0

the wheels. It has been possible to estimate this effect independently in the course of special tests carried out by means of the dynamometric tow-car built in France by the "Technical Auto Union" (U.T.A.C.)[15] and on which the wheels can be turned at will to a pre-determined angle.

The results obtained with natural rubber tires have been summarized in Figure 8.

The load on each tire was sensibly identical with that used on the car tests and the speed close to 60 km/hr. In accordance with wear values obtained in the course of these experiments it can be estimated that the average angle of turning on the Montlhéry road circuit is of the order of 3 to 4 degrees. The
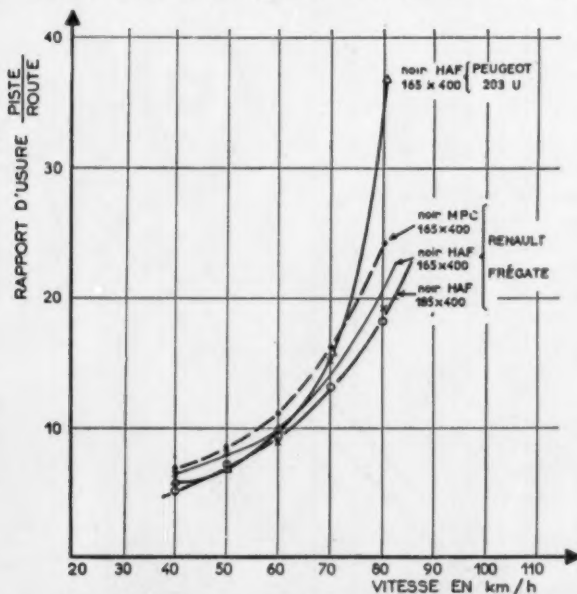
Fig. 9.—Relation between the wear (usure) on the race track and on the highway as a function of the speed (vitesse). *Noir* means black.

question can be raised whether the results of the tests made on this track correlate with those observed on the normal highway. To resolve this problem a series of experiments was made in which the same vehicles equipped with the same tires were driven at variable speeds alternately on the course Montlhéry-LaFlèche and on the road track of the Montlhéry race track. It may be seen from Table XII and Figure 9 that a certain relationship exists between the results obtained on the road and on the track and that for an average speed of 60 km/hr, there is between these two types of circuit a severity ratio approaching 10, practically independent of the type of tire and of the type of vehicle used.

THE POSSIBILITY OF A CORRELATION BETWEEN ROAD AND LABORATORY TESTS

In line with what precedes, the complexity of the factors which may affect the wear of pneumatic tires and the difficulties which may arise are measured

when one wants to evaluate the resistance to abrasion of an experimental
mixture.   This is why it has always been attempted to solve this evaluation
problem through tests made in the laboratory by means of abrasion machines.
Unfortunately, except for a few particular cases, the results obtained in this
manner seemed to be in complete disagreement with those obtained from
practical tests.   The existence of a certain possible correlation between the
road tests and the track tests, added to the fact that the wear ratios between
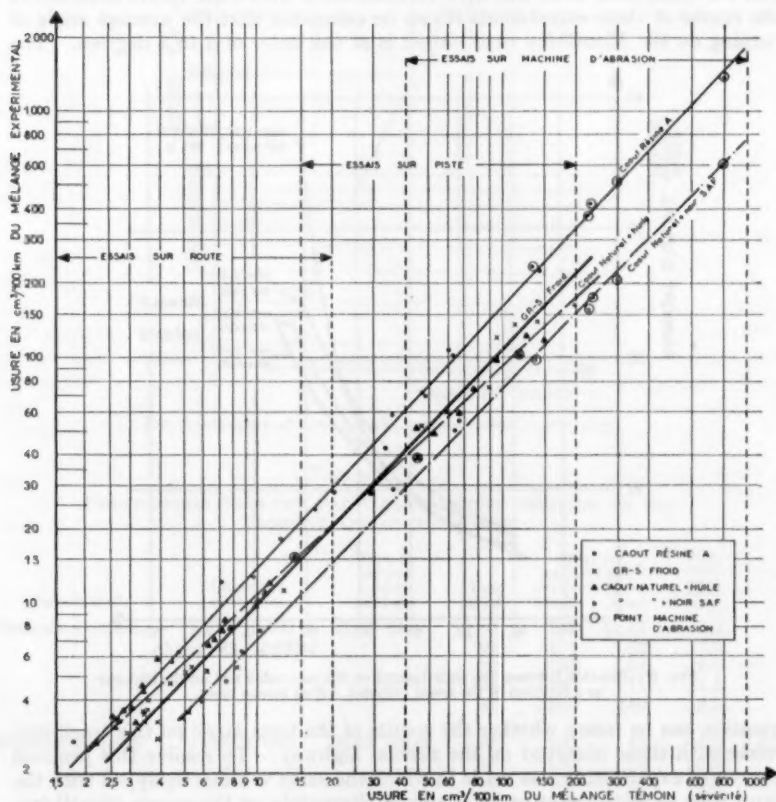
Fig. 10.—Wear-severity relationships for a few types of mixture.

different mixtures could be modified profoundly as a function of the severity of
the tests, led to an hypothesis according to which there was perhaps no discon-
tinuity between the different evaluations since the abrasion machines created
extremely severe conditions, of the order of 20 to 100 times those of the normal
road; only the severity vitiated the estimations.   To verify this idea, there has
been plotted as a function of the wear of the different reference mixtures (sever-
ity), the wear of the experimental mixture having served for the comparison.
One can see in Figure 10 that the experimental points recorded for types of

mixtures which are as different as the rubber-resin combinations, the mixtures loaded with different carbon blacks, the mixtures with a cold GR-S base, line up correctly as a function of the severity of the test, both for the tests on the road and the track, and on the laboratory abrasion machine.

The calculation of the correlation coefficients for these lines of regression has given figures exceeding 0.93. Tests are underway at present for the purpose of confirming these first results. They will probably be dealt with in a later paper.

The examination of Figure 10 may explain the inversions in classification observed between the road test results and the laboratory results. In fact, this classification, expressed by the ratio

$$U_r = \frac{\text{Wear of the experimental rubber}}{\text{Wear of the reference rubber}}$$

may be deduced directly from Figure 10 for any severity, by calculating the $\dfrac{\text{ordinate}}{\text{abscissa}}$ ratios.

It is seen that the values of these are dependent on the slope of the line expressing the correlation between the experimental mixture and its reference. One can thus understand that a mixture which gives interesting results on the abrasion machine (case of the rubber extended with oil) may show a behavior on the road which is not as good, or vice versa (case of the rubber-resin A mixture).

CONCLUSION

One can thus say that in the course of tire tests, all of the experimental conditions, whether they affect more particularly the wear by test period or by wheel position, influence the wear results.

Notwithstanding the complexity of these influences and of their interactions it has been possible to verify that a relation existed between the tests on special cars and those made on private cars commonly used by everyday users, and to establish a correlation between the normal road tests and accelerated tests on the track.

These studies have shown the importance of the severity of the tests for the estimation of the relative value of the mixtures and it has been possible to evaluate the influence of a certain number of factors on this severity which is, in reality, the resultant of the effects of all the experimental conditions on the wear of pneumatic tires.

The variations in relative wear of the mixtures as a function of the severity have led to the thought that a correlation might exist between the practical tests on the road or on the track and the experiments made in the laboratory with the aid of abrasion machines.

The existence of such a correlation is very important for it will permit an effective selection of the mixtures, destined for the manufacture of treads, in the research investigations. However, one must still look for a suitable adjustment of laboratory tests in order to obtain an estimation which is directly transposable to the complex domain of the pneumatic tire.

This simplification, however, will not bring about the disappearance of road tests for it will, after all, be necessary to make a few practical verifications, be it only for studying the road behavior of the experimental mixtures or their resistance to cracking.

This study has been made within the framework of the research programs of the Rubber-Stichting and of the French Rubber Institute, the study being in turn a part of the entirety of the investigations pursued under the protection of the International Rubber Research Board.

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FACTORS AFFECTING LABORATORY CUT-GROWTH
RESISTANCE OF COLD SBR TREAD STOCKS *

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The relatively poor groove cracking resistance of cold styrene-butadiene (SBR) tread stocks is one of their principal defects. Groove cracking failures in tires involve the process by which small cracks, initiated by sharp objects or by ozone, grow in size as the tire is repeatedly flexed in service. The mechanism of fatigue cracking failures of this type is not clearly understood. Consequently agreement on methods of measuring crack-growth resistance in the laboratory and on techniques for making tread compounds less susceptible to groove cracking is not easy to attain.

A completely satisfactory mechanism must explain such failures in terms of certain fundamental properties of the stock, such as the stress-strain properties, hysteresis, rate and extent of crystallization (if any) of the polymer during stretching, oxidation resistance, and the like.

A major obstacle to investigations of the mechanism of fatigue cracking of rubber compounds has been the lack of reproducibility of the available tests. Thus, uncontrolled variations in the properties of the individual test specimens, particularly in the degree of cure as measured by the modulus (stress at 300 per cent elongation), have been found in many cases to mask completely the effect of compounding variations. Similarly, uncontrolled variations in the testing procedure, such as differences in strain cycle due to slight irregularities in the way replicate samples are mounted in the test machine, further diminish the reproducibility of the test results. The difficulties involved in obtaining reproducible results in fatigue tests have been canvassed thoroughly by Buist[1] and by Buist and Williams[2] in recent reviews of the subject.

The modified De Mattia cut-growth test that has been used in the laboratories of U. S. Rubber[3] for many years also suffers from the defects characteristic of flexcracking tests in general. Recently, however, it has been found possible to utilize this test in such a way that results having increased reproducibility and significance can be obtained. Of even greater interest is the fact that, by means of the improved testing procedure, a deeper insight can be obtained into the mechanism by which groove cracking takes place in cold SBR tread stocks.

This paper reports the use of an improved testing technique to establish quantitative relations between cut-growth resistance and modulus, or between cut-growth resistance and ultimate elongation, of cold SBR stocks. Although the cut growth versus modulus function is of practical importance, a more fundamental relation holds that the cut-growth resistance of cold SBR black stocks is largely determined by their elongation at break, regardless of other properties.

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DETAILS OF THE IMPROVED CUT–GROWTH TEST

The use of the new testing procedure in determining cut-growth resistance involves no change in the method of making individual measurements by means of the modified De Mattia machine.   The sample and test conditions are shown in Figure 1.   One-inch-wide testpieces are cut from a molded slab 6 × 3 × 0.375 inch, with a U-shaped groove 0.187 inch deep.   Prior to testing, the center of the groove is pierced through with a needle 0.037 inch in diameter in order to initiate a cut.   The samples are then flexed through an angle of 85 degrees at the rate of 287 cycles per minute until the cuts have grown to approximately 0.5 inch in length.   The machine is so adjusted that the testpieces are in a position of zero strain at the beginning of each flexing cycle.   The results obtained at room temperature (80 ± 5° F) and 150 ± 3° F are expressed as cut-growth resistance in kilocycles of flexing per inch of crack growth.

The usual method of characterizing the cut-growth resistance of a stock is to average the results obtained on a number of testpieces that have a state of cure
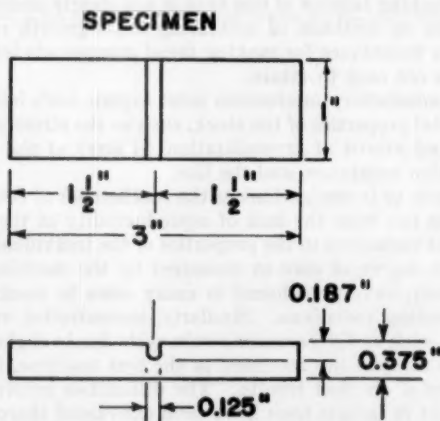
SPECIMEN

Fig. 1.—Details of specimen used by U. S. Rubber for determining flex-cracking resistance on the modified De Mattia machine.   Test conditions are as follows: angle of bend, 0 to 85 degrees; frequency, 287 cycles/min; temperature, 80 to 150° F; piercing needle, 0.037 inch in diameter.

considered optimum for the intended use of the compound under investigation. The reproducibility of such results usually is poor; an important cause is the difficulty of securing a precisely defined, highly reproducible state of cure. Even slight cure variations may produce large variations in the cut-growth resistance of the testpieces, and this point is especially true of SBR stocks, whose fatigue properties are very sensitive to the state of cure.

The improved method, developed primarily for the purpose of minimizing the effect of uncontrolled variations in the state of cure, consists of determining the cut-growth resistance of each formulation over a very wide range of cures. The results are then plotted against some physical measure of the state of cure. When the modulus (stress at 300 per cent elongation) is used as a measure of the state of cure, there results from every such test a band of points, each of which represents the cut-growth resistance and the modulus of an individual testpiece.   In spite of the error inherent in individual cut-growth measure-

ments, it has been found that a curve fitted either graphically or by the method of least squares to the data thus obtained has a fairly high degree of reproducibility. From such a curve, the cut-growth resistance of a stock can be determined at any desired modulus value, with greater precision and significance than was possible previously.

In using the new method, modulus values are obtained in the usual manner on testpieces cut from slabs $6 \times 6 \times 0.1$ inch that are prepared along with the cut-growth samples. Swelling measurements have shown that the modulus of the tensile test slabs is virtually identical with that of the rubber in the grooved region of identically compounded and cured cut-growth testpieces.

RELATION BETWEEN CUT–GROWTH RESISTANCE AND MODULUS

Although the primary purpose for developing the new testing procedure was simply to improve the reproducibility and increase the significance of cut-growth measurements, it soon became apparent that through this technique a relation between cut-growth resistance and modulus is disclosed that is in itself quite important and that could be used to study other factors which affect cracking.

TABLE I
COLD SBR COMPOUNDS

SBR 1500	100
Carbon black	52
Softener	6
Stearic acid	1
Zinc oxide	3
N,N'-diphenyl-p-phenylene diamine (JZF)	0.35
Mercaptobenzothiazole	0.6 to 1.0
Diphenylguanidine	0.3 to 0.6
Sulfur	1.0 to 3.5

Blacks: HMF, FEF, HAF, SAF
Cure: 30 to 120 minutes at 274° F.

For example, a conventional cold SBR tread stock containing 52 parts of a high abrasion furnace black was cured to various modulus levels as shown in Table I. Modulus variations were obtained by varying the amounts of accelerator and sulfur and the curing time, separately or together. A semilogarithmic plot of the cut-growth resistance (kilocycles per inch growth) versus the 300 per cent modulus is shown in Figure 2. The results obtained at room temperature fall within a well-defined band; while the results obtained at 150° F fall within a lower band. In each case the plot is nearly linear over the modulus range of 800–2800 psi, so that within this range the results can be expressed by the relation

$$\log (KC/\text{in}) = a - b(M) \tag{1}$$

where: KC/in = cut growth resistance in kilocycles per inch. $M = 300$ per cent modulus in pounds per square inch. a and b are parameters which are constants for a given stock at a given temperature.

The cut-growth resistance of SBR tread stocks has long been known to decrease with increasing cure, but by determining cut-growth resistance as a function of modulus over a wide range of cures, the logarithmic nature of the decrease becomes clearly evident. The data also reveal an unsuspected maximum in the cut growth versus modulus relation and indicate that the cut-growth resistance

of a SBR/HAF tread stock may be adversely affected if the state of cure is reduced to too low a value.

Similar curves, but with different parameters, are obtained using equilibrium modulus values measured at 300 per cent or 100 per cent elongation. For simplicity, however, first pull values at 300 per cent extension were used in all data reported here.

From the data in Figure 2 and from similar data at other temperatures, the temperature coefficient of crack propagation can be determined at any modulus level. Thus at a modulus of 1200 psi the rate of crack growth approximately doubles with every 21° F (12° C) rise in temperature between 80° and 150° F,
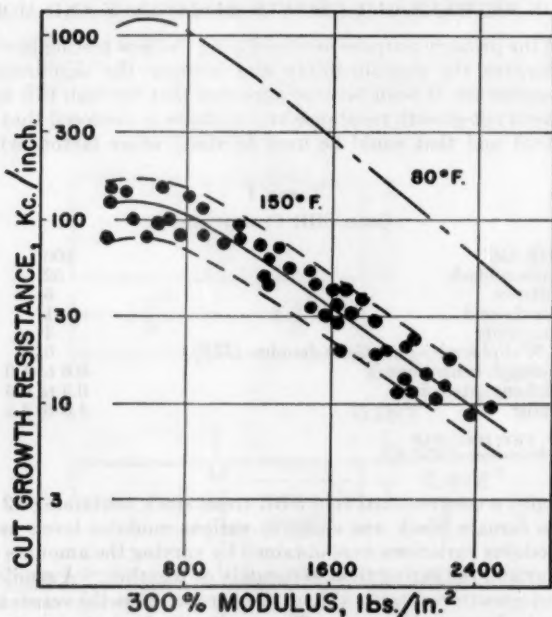
Fig. 2.—Cut-growth resistance versus 300 per cent modulus for SBR stock containing 52 phr HAF black.

and the cut-growth resistance at 150° F is only about 1/10 that at 80° F. This temperature coefficient agrees well with that recently obtained by Buist[1] for SBR tread stocks with a Flipper machine[4]. The temperature coefficient varies somewhat with the modulus and, at any given modulus value, with the type of filler used.

INSENSITIVITY OF CUT GROWTH–MODULUS RELATION TO COMPOUNDING AND CURING VARIABLES

To obtain the extensive modulus variations required by the procedure described above, it is necessary to vary the accelerator and sulfur concentrations in the stock or the curing time, individually or simultaneously. The question

TABLE II

CURING SYSTEMS FOR SBR/HAF BLACK STOCK

SBR 1500	100
HAF black	52
Softener	6
Stearic acid	1
Zinc oxide	3

	Conventional	Low sulfur	Tuex
Mercaptobenzothiazole	0.6–1.0	—	—
Diphenylguanidine	0.3–0.6	—	—
Tetramethylthiuram sulfide	—	1.5	—
Sulfur	1.0–3.5	0.35–1.25	—
Tetramethylthiuram disulfide	—	—	1.5–10.0

Cure: 30 to 120 minutes at 274° F.
15 to 90 minutes at 293° F.

immediately arises as to whether these curing variations themselves influence the cut-growth resistance of the vulcanizates. Generally speaking, a SBR stock can be brought to a given modulus by using any one of a variety of curing systems and curing conditions in conjunction with one another. If however, the cut-growth resistance corresponding to a given modulus depends upon the way in which the modulus is obtained, it is clear that reproducible relations between cut-growth resistance and modulus will be difficult to obtain.

For this reason it was necessary to compare the cut-growth versus modulus
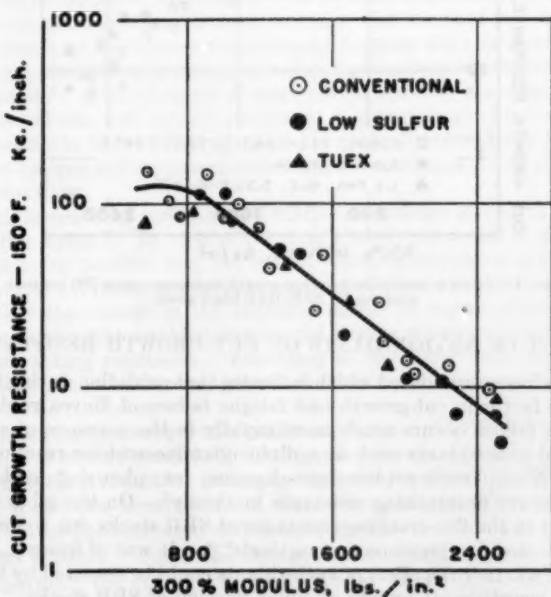
FIG. 3.—Effect of type of cure on cut-growth resistance versus 300 per cent modulus for SBR tread stock.

relations of tread stocks that were identical except for the method used to vary
the modulus.   These cold SBR stocks were all prepared from the same master-
batch containing 52 parts of high abrasion furnace (HAF) black.   The formula-
tions, shown in Table II include: (a) a conventional curing system with varying
amounts of sulfur and accelerator and varying curing times and temperatures;
(b) a highly efficient low sulfur vulcanizing system with a high accelerator con-
tent and with varying sulfur levels and curing times; (c) a non-sulfur curing
system using tetramethylthiuram disulfide, with varying curative levels and
curing times.

Figure 3 shows that, within the limits of experimental error, the cut growth
versus modulus relations for any given tread stock is independent of wide varia-
tions in the curing system and in the curing conditions.
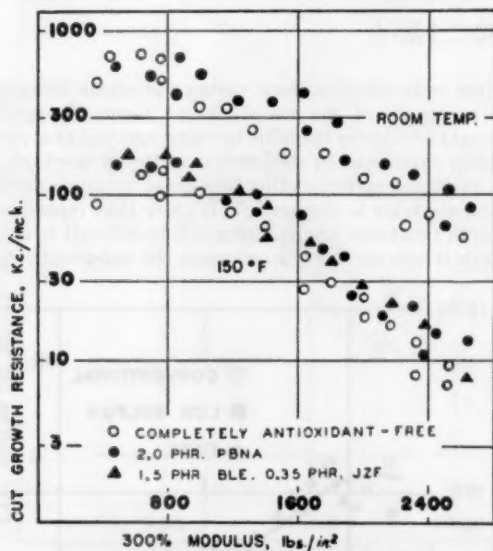
Fig. 4.—Effect of antioxidants on cut-growth resistance versus 300 per cent
modulus for SBR/HAF black stock.

EFFECT OF ANTIOXIDANTS ON CUT–GROWTH RESISTANCE

Evidence has accumulated which indicates that oxidation during flexing is a
contributing factor in cut-growth and fatigue failure of Hevea rubber stocks.
Flexcracking failure occurs much more rapidly in the presence of air than in
nitrogen, and antioxidants such as a diphenylamine-acetone reaction product
(BLE), N, N'-diphenyl-p-phenylene-diamine, or phenyl-2-naphthylamine
(PBNA) improve flexcracking resistance markedly[5].   On the other hand, any
improvement in the flex-cracking resistance of SBR stocks due to antioxidants
was not detected by previous test methods[6-8].   It was of interest, therefore,
to determine whether the effect of antioxidants could be detected by their effect
on the more sensitive cut growth-modulus relation of SBR stocks.

In one set of experiments, PBNA or BLE in combination with JZF were
added to an antioxidant-free SBR containing 52 parts of HAF black.   The

polymer used was a special batch coagulated and dried at low temperature in order to prevent gel formation, since the presence of gel as a result of inadequate stabilization of SBR has been shown to reduce cut-growth resistance[6]. The stocks were cured by the vulcanizing system shown in Table I, and the amounts of antioxidants are shown in Figure 4. Modulus range was obtained by varying sulfur from 1.0 to 3.5 parts.

The results obtained at room temperature, shown in Figure 4, reveal a slight, but significant upward shift in the plot of log $KC/$in versus modulus, due to the incorporation of antioxidants. A smaller shift is observed for results obtained at 150° F. Thus, addition of small amounts of antioxidants improved very slightly the cut-growth resistance of otherwise antioxidant-free cold SBR tread stocks. In other experiments, not shown in detail, the addition of up to 4.0 parts of PBNA to a stock already containing the normal amount of antioxidant gave no further improvement in the cut-growth resistance.

These observations lead to the conclusion that the oxidation of SBR in the growing crack during the cut-growth test is not an important factor in crack propagation, in contrast to the behavior of natural rubber. The absence of specific effects of antioxidants on cut-growth resistance of unaged SBR vulcanizates is in agreement with the previously cited observations.

INSENSITIVITY OF THE CUT GROWTH–MODULUS RELATION TO AGING

During air aging at elevated temperatures, several chemical reactions affecting the modulus of rubber compounds occur simultaneously. Some of the reactions tend to increase the modulus. Among these are the formation of new crosslinks due to oxidation reactions and the formation of additional sulfur crosslinks due to combination of residual free sulfur with the rubber. On the other hand, chain-scission reactions simultaneously decrease the modulus.

In the case of SBR vulcanizates, crosslinking reactions which increase modulus predominate[9]. This physical change reflects not only a net increase in the density of crosslinks, but, equally important, a change in the kind of crosslinks. The new crosslinks formed during aging are generally considered to consist of both carbon-oxygen and carbon-carbon bonds, formed as a result of free radical oxidation reactions.

The fatigue-cracking resistance of SBR vulcanizates is known to decrease rapidly during aging[10]. In view of the data already presented in this paper, it would seem quite possible that the loss of cracking resistance during aging is simply a function of the increase in the modulus of the stock. It is also possible, however, that the change in the chemical nature of the crosslinked network referred to above might establish in the aged stock a structure that is inherently poor in flexcracking resistance. According to the latter view, an aged stock would exhibit a much lower cut-growth resistance than does an unaged stock having the same modulus.

By determining the cut growth-modulus relations of SBR stocks before anp after aging, it is readily possible to distinguish between these two mechanisms. If the loss in fatigue resistance during aging is due simply to the increase in the number of crosslinks, irrespective of their chemical character, then the cut-growth resistance for both aged and unaged stocks will obey the same logarithmic modulus relation. But if the change in the chemical nature of the crosslinks is important, the cut-growth resistance for aged stocks will deviate significantly from that of unaged stocks having the same modulus.

Such an investigation was carried out on the SBR tread stock containing

52 phr of HAF black, shown in Table I.   Cut-growth resistance was determined as a function of modulus for unaged vulcanizates and for the same stocks after two and four weeks of aging in circulating air at 158° F (Geer aging).   The data shown in Figure 5 reveal that as aging progressed, the modulus of the vulcanizates increased markedly, but the cut-growth resistance was affected only to the extent that the modulus increased.   After the samples were aged two and four weeks, the plot of log (KC/in) versus 300 per cent stress coincides with that characterizing the unaged samples.   During Geer aging, changes in the chemical nature of the network structure of the vulcanizate evidently have no effect on cut growth in this SBR formulation.   Similar results have been obtained in studies of other types of SBR tread stocks.
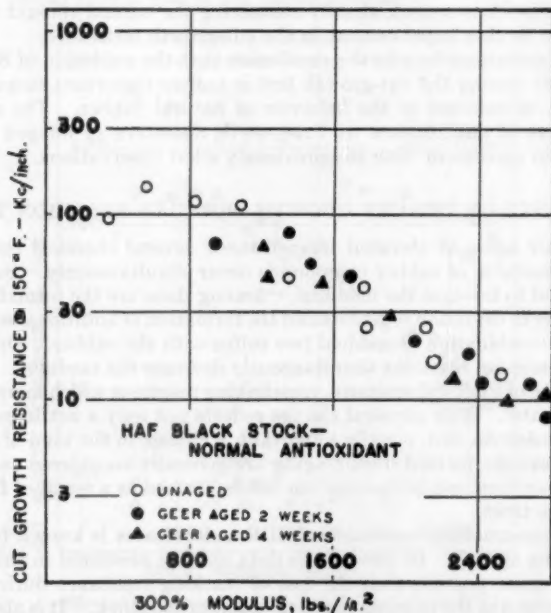
FIG. 5.—Effect of Geer aging on cut-growth resistance versus 300 per cent modulus for SBR/HAF black stock containing normal antioxidant.

The insensitivity of the cut growth-modulus relations to aging, however, might be due to the effect of antioxidant in the stock.   As aging progresses, the concentration of antioxidants originally present gradually decreases, but it seemed possible that even after several weeks of Geer aging, enough residual antioxidant might remain to affect the nature of the results.   The preceding experiment was therefore repeated with the specially prepared stock completely free of antioxidant, described in the preceding section.   The cut growth-modulus relation was determined before aging and after two and four weeks of Geer aging.   The results, shown in Figure 6, are similar to those obtained with stocks containing a normal amount of antioxidant, shown in Figure 5.   Thus in both cases the effect of Geer aging on cut-growth is that caused by the increase

in modulus, and the benefit of antioxidant stabilizers on the cut-growth resistance of SBR vulcanizates is due only to the prevention of inordinately large increases in modulus.

VARIOUS TYPES OF CARBON BLACKS IN COLD SBR TREAD STOCKS

The improved testing techinque was employed in a comparison of different types of carbon black in cold SBR tread stocks. Formulations involving four different types of furnace blacks at loadings of 52 phr, but otherwise similar, are shown in Table I. In each case variations in the modulus over a very wide
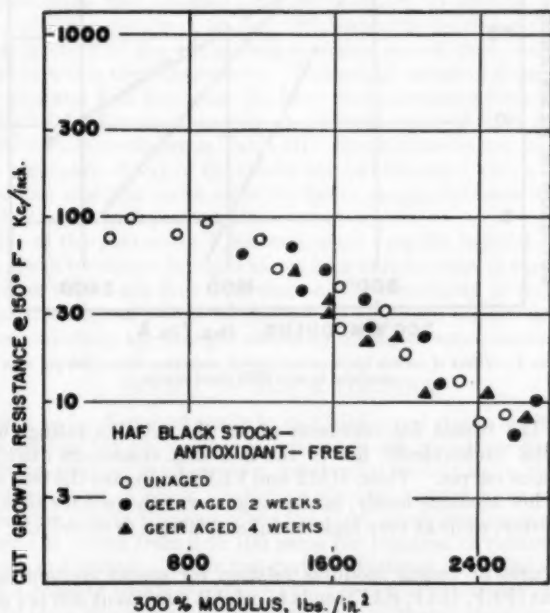
Fig. 6.—Effect of Geer aging on cut-growth resistance versus 300 per cent modulus for SBR/HAF black stock containing no antioxidant.

range were obtained by varying the acceleration, sulfur, and the curing time. A single blend of SBR was used for all masterbatches. Carbon black, zinc oxide, and softeners were incorporated in a laboratory "B" Banbury mixer; the discharge temperature, after a 10 minute mixing cycle, was 285–300° F. The remaining ingredients were incorporated on a mill.

Figure 7 shows the cut growth versus modulus curves obtained at 150° F for each of the formulations of Table I. It will be understood that each curve represents a band of data similar to those in Figures 2–6. The results show that in the modulus range of 800–2800 psi each type of black gives a logarithmic relation between cut-growth resistance and modulus, of the type represented by Equation (1). Different blacks, however, give curves with different slopes; so the relative ratings of the compounds depend upon the modulus at which they are
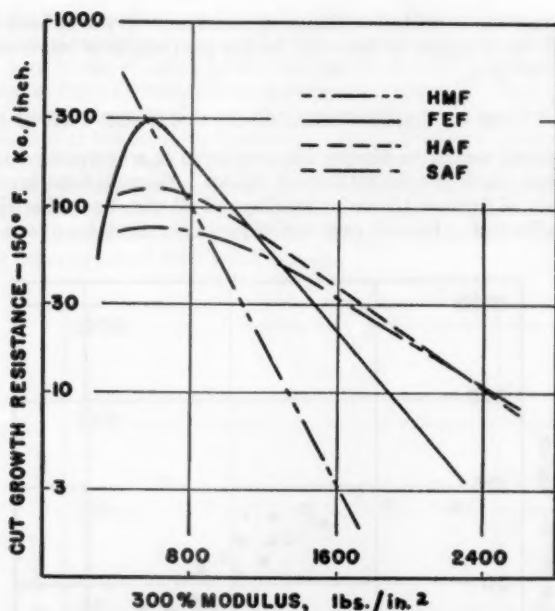
Fig. 7.—Effect of carbon black on cut-growth resistance versus 300 per cent modulus in cold SBR tread stocks.

compared. The reason for confusion about the relative ratings of different blacks in SBR undoubtedly lies in the fact that crossovers exist in the cut growth-modulus curves. Thus, HMF and FEF blacks give the best cut-growth resistance at low modulus levels; in the range normally used for tires, HAF and SAF are superior; while at very high modulus (2000 psi or more) SAF black may be best.

The cut growth versus modulus relation for stocks containing the finer furnace blacks (FEF, HAF, SAF) tends to exhibit maxima at 300 per cent moduli

TABLE III

SLOPES AND INTERCEPTS OF CUT GROWTH–MODULUS CURVES FOR DIFFERENT BLACKS*

	Value of parameters			
	At room temperature		At 150° F	
Black	a	b($\times 10^9$)	a	b($\times 10^9$)
HMF (Kosmos 40)	4.17	1.47	3.52	1.90
FEF (Philblack A)	4.57	1.29	3.20	1.16
EPC (Wyex)	3.39	0.91	2.44	0.77
MPC (Spheron No. 6)	3.77	1.12	2.39	0.68
HAF (Philblack O)	3.67	0.74	2.59	0.64
SAF (Philblack E)	3.11	0.58	2.44	0.59

* Values of the parameters, a and b, Equation (1), for linear portion of curves. Blacks listed in order of decreasing values of b at 150° F.

in the vicinity of 600 psi. For these stocks the linear logarithmic relation between cut growth and modulus appears to break down at low modulus values. For stocks that contain larger particle size blacks, such as SRF (semi-reinforcing furnace), there is usually no breakdown in the linear relation, even at very low modulus. These observations will receive more attention later on.

Although not shown in Figure 7, the curves representing the cut-growth behavior of the different blacks at room temperature are, generally speaking, similar to those obtained at 150° F except that the cut-growth resistance values obtained at any given modulus level are roughly 7 to 10 times as great at room temperature as they are at 150° F.

The experiments just described can be extended to include other blacks. The blacks tested can then be compared with respect to the slopes and intercepts of the linear portion of the cut growth-modulus curves that characterize the formulations in which they are present. Numerical values of these parameters, designated as a and b in Equation (1), have been calculated both at room temperature and 150° F for stocks having six different types of black at loadings of 52 phr. The results are shown in Table III. From these values, the laboratory cut-growth resistance of any of the stocks can be calculated with a fair degree of accuracy at any modulus value over the linear range (between 800–2800 psi) through substitution in Equation (1).

The value of the parameter, b, shows in each case the logarithmic decrease in the cut-growth resistance brought about by a unit increase in the 300 per cent modulus; these values are thus a measure of the sensitivity of the cut-growth resistance of the various stocks to changes in modulus, regardless of whether the modulus variations are brought about by curing or aging mechanisms.

EFFECT OF BLACK LOADING

The results so far discussed apply to cold SBR tread stocks having a conventional black loading (52 phr). It is of interest to determine how the cut growth versus modulus relation is affected by substantial variations in black loading. Although other types of black (including channel blacks) have been investigated as well, the results obtained when the HAF black loading in the formulation of Table I is varied from 0 to 100 parts per hundred of rubber are typical and are shown in Figure 8. When cut-growth resistance is plotted as a function of modulus, a band of points is obtained that is characteristic for each loading. These bands (and the curves which are fitted to them) show an interesting progression which covers a very great range of cut-growth values as the black loading and the modulus are varied from very low to very high values. For modulus levels in excess of 1000 psi each curve approximates the relation expressed by Equation (1), except that the parameters, a and b, vary greatly with black loading.

At low black loadings this linear logarithmic relation holds true down to the lowest modulus levels that were obtained experimentally. At a black loading of 52 phr, however, the linear relation appears to break down at low modulus values. At black loadings of 80 and 100 phr the linear relations are transformed into curves with well defined maxima followed by a sharp decrease in cut-growth resistance as the modulus is progressively decreased below about 1000 psi.

The curves of Figure 8 can be used to determine the cut-growth resistance as a function of the loading of HAF black at any modulus level. Constructed with data taken from Figure 8, Figure 9 shows cut-growth resistance as a function of black loading for modulus levels of 800, 1200, and 1600 psi; a separate
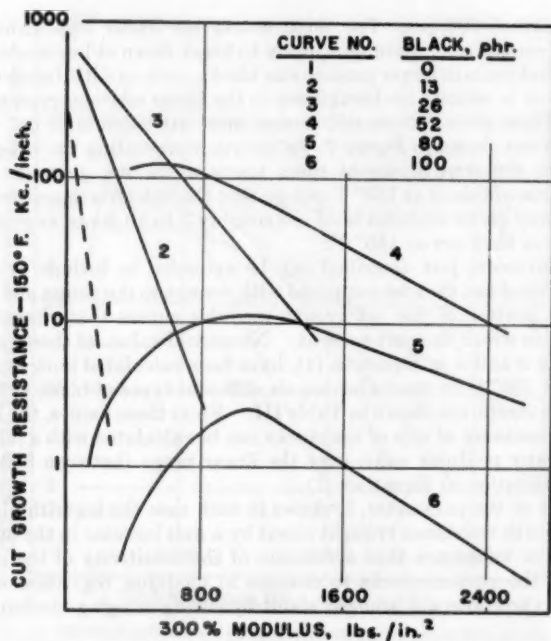
FIG. 8.—Effect of HAF black loading on cut-growth resistance versus 300 per cent modulus.
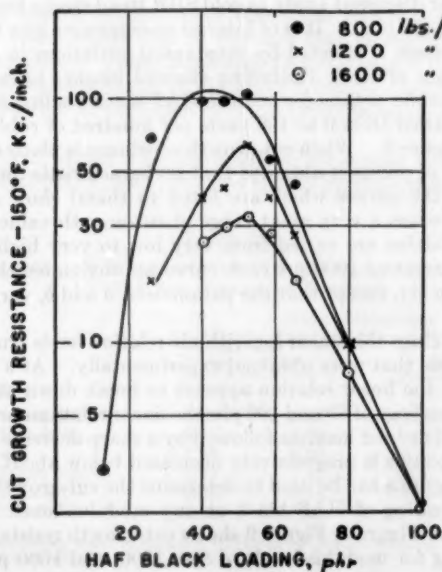
FIG. 9.—Cut-growth resistance as a function of HAF black loading at various 300 per cent moduli.

curve is obtained at each modulus.   These curves reveal that for any given modulus level there exists a narrow range of black loadings within which the cut-growth resistance of the vulcanizates is a maximum.   For SBR/HAF stocks having a normal tire cure, this optimum range lies between approximately 45 and 55 phr of black.   Groove-cracking resistance decreases rapidly as the black loading departs, in either direction, from this range.

From a theoretical point of view it seems perhaps surprising that the curves of Figure 9 should exhibit maxima.   It is possible, however, to demonstrate that the form of these curves is directly related to the stress-strain characteristics of the stock.   The explanation arises from the connection that has been
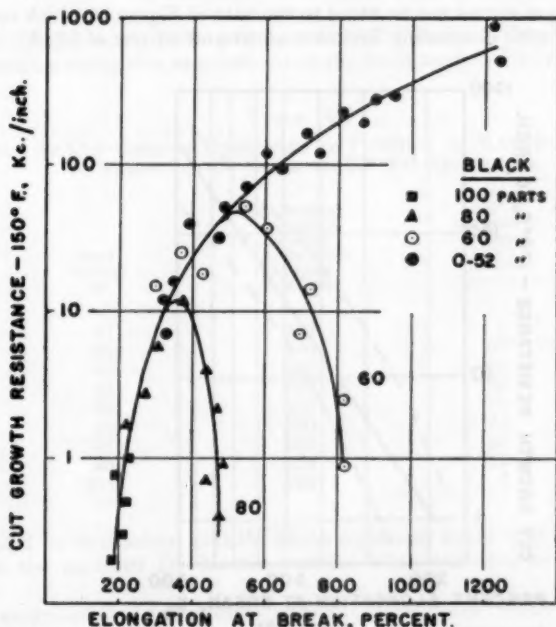
FIG. 10.—Cut-growth resistance versus elongation at break for SBR/HAF black stocks.

found to exist between the cut-growth resistance and the breaking elongation. This new relation will now be considered.

CUT–GROWTH RESISTANCE IN RELATION TO ELONGATION AT BREAK

The relation between cut-growth resistance and modulus in cold SBR stocks at 150° F has been shown to be dependent on the type of black used and greatly dependent on the black loading.   On the other hand, the relation has been found to be virtually independent of substantial variations in the curing system, temperature and time of cure, antioxidant concentration, extent of air aging, etc.   These conclusions suggest that the cut-growth resistance of SBR stocks, although related to their moduli, may be even more fundamentally related to some other physical property, in terms of which there will result an

expression for cut-growth resistance that is independent of the type of black and the black loading.

Figure 10 shows that such a property is the elongation at break measured at room temperature. If the cut-growth values used in obtaining Figure 8 are plotted aginst the breaking elongation of the corresponding vulcanizates instead of against their 300 per cent modulus values, the data for the varying black loadings all fall within one single band, independent of black loading (if, for the moment, we exclude the data for stocks having very high black loadings *and also* very low cures). Although the data shown in Figure 10 are for SBR/HAF stocks, the relation there indicated has been shown to be essentially independent of the type of black used.

A system of curves can be fitted to the data of Figure 10 which consists of a main spine, with descending branches at 60 and 80 phr of black. These de-

EQUATION OF LINE= $\log \left(\frac{kc}{in.} \right) = 3.65 \log E_b - 8.31$
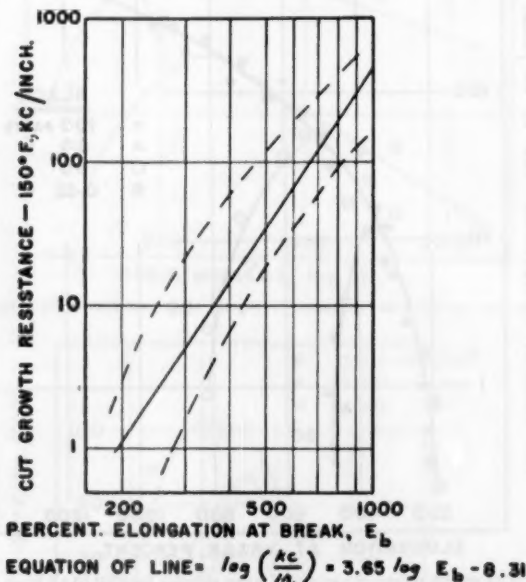
Fig. 11.—Cut-growth resistance versus elongation at break as log-log plot.

scending branches are caused by highly loaded stocks cured to very low moduli and reflect the deviations of the corresponding cut-growth versus modulus curves from the logarithmic relation (Figure 8). Actually, the cut growth versus elongation relation for the stock having 100 phr of black also has a descending branch, but the latter falls within the band characterizing the main spine.

The behavior of stocks with high loadings and also low states of cure suggests that the main spine of Figure 10 actually represents the envelope of a series of cut-growth versus breaking elongation curves, each of which passes through a maximum as the breaking elongation diminishes from a high value (at a low state of cure) to a low value (at a high state of cure). The location of these

maxima seems to move to the right along the envelope as the black loading diminishes. For black loadings of 50 phr or less, the location of the maxima presumably occurs at such low states of cure as to be virtually impossible to detect experimentally.

When black stocks, regardless of black loading, are all cured to a 300 per cent modulus of 800 psi or more, the descending limbs do not appear, and the cut growth versus breaking elongation data all fall within the main band of Figure 10. Figure 11 shows that on a log-log plot, this band is almost linear. It can then be approximately represented by a straight line having the equation:

$$\log (KC/\text{in}) = 3.65 \log E_b - 8.31 \tag{2}$$

where: (KC/in) = cut growth resistance at 150° F in kilocycles per inch. E_b = the breaking elongation as measured on the Scott machine[11] at room temperature.

TABLE IV

CALCULATION OF CUT–GROWTH RESISTANCE AS FUNCTION OF HAF BLACK LOADING IN TREAD STOCKS CURED TO 800 PSI MODULUS

Black loading, phr	% Breaking elongation of stock when 300% modulus is 800 psi	Calculated 150° F cut-growth resistance in kilocycles per inch (Equation (3))
0	—	—
13	320	7
26	540	46
40	650	91
46	640	86
52	625	79
58	590	64
65	500	35
80	375	12
100	230	2

It should be emphasized that the above equations apply only to results obtained on the modified De Mattia machine when operated as indicated in Figure 1.

It is recognized that correlations between crack-growth resistance measured at 150° F have been made with stress-strain properties measured at room temperature. If cracking resistance and stress-strain measurements were both made at the same temperature, the constants shown in Equation (2) would undoubtedly be altered somewhat; also, the experimental data might more closely approximate a linear relation on the log-log plot.

CALCULATION OF CUT–GROWTH RESISTANCE FROM MEASUREMENTS OF ELONGATION AT BREAK

Equation (2) signifies that the cut-growth resistance of any cold SBR tread stock in this test can be calculated if the breaking elongation of the stock is known. While this statement applies without qualification only if stocks having both very high black loadings and very low states of cure are excluded, it holds for all practical tread vulcanizates since these are usually cured to 300 per cent modulus values of 800 psi or more.

Equation (2) can be used to explain the maxima which characterized the curves of Figure 9. Thus, the procedure for calculating the cut-growth resistance as a function of carbon black loading in cold SBR/HAF tread stocks cured to a 300 per cent modulus of 800 psi is summarized in Table IV, and the results are shown in Figure 12.

The first step is to determine, over a wide range of cures, the stress-strain properties of stocks having varying amounts of HAF black. The 300 per cent modulus is then plotted against the breaking elongation, as shown in Figure 12A. From each of these curves, the breaking elongation that corresponds to a 300 per cent modulus of 800 psi is then determined. Finally, these breaking elongations are substituted into Equation (2), and the calculated cut-growth resistance values are plotted against the corresponding black loadings, as indicated in the curve in Figure 12B. This curve is seen to have the general features
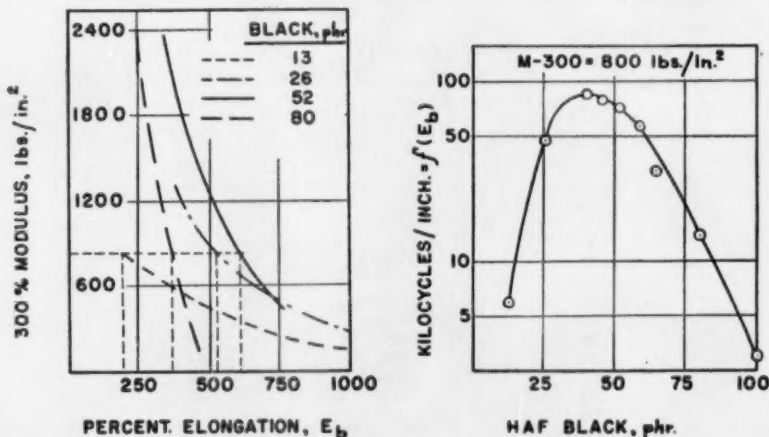
Fig. 12.—A, *left*, 300 per cent modulus versus elongation at break—effect of HAF black loading; B, *right*, calculated cut-growth resistance versus HAF black loading

of the corresponding curve in Figure 9, and the calculated cut-growth resistance values do not differ greatly from those obtained experimentally.

SUMMARY AND CONCLUSIONS

By using an existing cut-growth test in a new way it has been possible not only to increase the reproducibility of the results, but also to show important relations between cut-growth resistance and modulus, or the elongation at break of cold SBR tread stocks.

The logarithm of the cut-growth resistance of cold SBR vulcanizates as measured on a modified De Mattia machine, is shown to be a linear function of the 300 per cent modulus, except for certain undercured stocks. The slope of the curve is dependent on the type and the amount of black, but is relatively independent of the type of curing system, amount of antioxidant, and time of Geer aging.

An equation has been found which relates cut-growth resistance at 150° F with the elongation at break of the vulcanizate. Except for stocks having black

loadings in excess of about 55 phr and having in addition modulus values less than 800 psi, this relation appears to be nearly independent of black loading, type of black, curing system, time or temperature of cure, antioxidant concentration, and extent of Geer aging.

The elongation at break of an SBR tread stock thus appears to be a primary factor governing its groove-cracking behavior. The relation between cut-growth resistance and modulus is of secondary significance and evidently depends upon the interrelation between the modulus and breaking elongation of these formulations. The breaking elongation, however, cannot be the sole factor governing the groove-cracking behavior; otherwise there would be no restrictions on the validity of the breaking elongation equation.

ACKNOWLEDGMENTS

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CONTRIBUTIONS TO THE MECHANISM OF DEVULCANIZATION II *

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INTRODUCTION

A previous communication[1] recorded certain chemical changes which take place as a result of the reclaiming of three different types of natural rubber vulcanizates. The findings are summarized as follows:

1. According to the reclaiming process used, there are varying degrees of increase in the zinc sulfide content, and under certain specific conditions, i.e., alkali treatment or prior removal of uncombined sulfur, there is a small but definite decrease in sulfur combined to rubber.

2. It is well known that reclaim RHC contains a depolymerized fraction which is soluble in chloroform, and some earlier publications have inferred a value of between 7 and 10 for the ratio of the sulfur percentage in the chloroform insoluble rubber hydrocarbon to that in the chloroform soluble fraction. Our work shows this ratio to be only of the order of 1.05 to 1.44, for reclaims from normal sulfur-cured vulcanizates, and 2.0 to 2.4 for a sulfurless TMT type.

While it is appreciated that our investigation was not based upon orthodox commercial reclaims, and that higher temperatures are used today in reclaiming, the concept that the soluble fraction of the reclaim hydrocarbon is relatively sulfur-free can no longer be accepted.

3. Sulfurless TMT vulcanizates, a class normally accepted as nonreverting, were found to be the most amenable to plasticization under reclaiming conditions.

The work now presented covers some selected experiments in the reclaiming of natural, GR-S, and butyl rubbers. In order to investigate the degree of degradation which is seemingly inevitable in the thermal plasticization of vulcanized rubber, certain physical properties of the resultant reclaims were compared with those of the parent stocks. Degradation in this sense is used to express the differences in tensile strength, etc., of the cured reclaims, compared with their parent vulcanizates.

EXPERIMENTAL

Continuing the work on natural rubber, but using a type of accelerator containing no sulfur, the following compound was mixed and cured to optimum for 20 minutes at 140° C in the press.

Mix H

Smoked sheet	100.0
Zinc oxide	6.0
Sulfur	2.0
Stearic acid	0.5
Trimene base	1.5

The cured slabs were reclaimed as follows:

A. Fine ground, devulcanized in 3 per cent caustic soda for 24 hours at 191° C, washed with water, vacuum dried, and milled.

B. Fine ground, boiled with dilute sodium sulfite to remove free sulfur and, after washing, devulcanized in water for 24 hours at 191° C, and subsequently treated as in A. (See Table I.)

DISCUSSION

These results provide additional evidence that with alkali reclaiming, as well as when free sulfur is first removed with sodium sulfite, there is some reduction in rubber combined sulfur. The ratios $\frac{Q}{P}$ using 2 per cent sulfur and 1.5 per cent Trimene Base, as compared with those reported in our previous communication using a system 3.5 per cent sulfur and 0.5 per cent MBT, are as follows:

Treatment	Trimene base/ Sulfur	MBT/ Sulfur
Alkali reclaimed	1.09	1.18
Free sulfur prior removed with sodium sulfite and then re- claimed in water	1.34	1.42

A commercial alkali reclaim, prepared from latex scrap, was analyzed and the ratio $\frac{Q}{P}$ came out at 1.44. Within the limits of our experiments, therefore, the ratio of sulfur in the chloroform insoluble to that of the soluble fraction of the RHC of the reclaim does not vary widely with the vulcanizing system of the parent vulcanizate. Should this be generally true, it follows that this ratio is probably of less importance as an indication of certain suggested degradation mechanisms than was hitherto suggested.

RECLAIMING OF GR-S

The work here reported was confined to a simple mix using a phenolic sulfide as reclaiming agent and dipentene as swelling agent. The use of similar agencies has been reported previously in the literature[2].

Mix I	
GR-S	100
Zinc oxide	5
Stearic acid	2
Sulfur	2
MBTS	1

Slabs were cured for one hour at 137° C and then ground and devulcanized in water for 16 hours at 191° C, as follows:

1. Without further additions.
2. With varying ratios of reclaiming agent and 15 per cent Dipentene. Stocks were washed, dried and milled as previously. (See Table II.)

Rubber combined sulfur was computed from the total sulfur after acetone and alcoholic potash extractions, less sulfide sulfur.

TABLE I

Treatment	Total sulfur	Acetone extract	Sulfur in acetone extract	Sulfide sulfur	CHCl₃ Extract	$\dfrac{\text{S in CHCl}_3\text{ Ext.}}{\text{CHCl}_3\text{ sol. rubber}} \times 100$ (=F)	$\dfrac{\text{S in CHCl}_3\text{ insol. rubber}}{\text{CHCl}_3\text{ insol. rubber}} \times 100$ (=Q)	Q/P	% Sulfur combined to rubber
Mix H cured to optimum As above—desulfurised with sodium sulfite and well washed	1.82	3.56	0.32	0.36	1.29	—	—	—	1.12
Deulfurised as above. Devulcanized in water 24 hr at 191° C	1.44	6.08	0.03	0.36	1.37	—	—	—	1.12
Original Mix H alkali devulcanised 24 hr at 191° C	1.44	5.50	0.04	0.60	19.10	0.74	0.99	1.34	0.92
	1.62	2.56	0.04	0.95	19.16	0.70	0.76	1.09	0.74

TABLE II

Treatment	Total sulfur	Sulfide sulfur	Ash	Acetone extract	Sulfur in acetone extract	Alcoholic potash extract	Residual sulfur after alcoholic potash extraction	% sulfur combined to rubber
Mix I cured to optimum	2.19	0.18	5.7	12.2	0.32	2.21	1.84	2.12
As above—devulcanized in water only for 16 hr at 191° C	2.15	0.29	5.3	11.6	0.30	2.50	1.86	2.00
As above—with excess reclaiming agent and 15% dipentene. Devulcanized in water for 16 hr at 191° C	3.16	1.14	5.3	15.5	0.38	3.60	2.66	2.06

DISCUSSION

1. Cook, et al.[2] have investigated the use of certain polyalkyl phenolic sulfides in the reclamation of vulcanized GR-S. In their presence they found a small though definite increase in rubber combined sulfur, whereas without reclaiming agent, this was slightly reduced. In our experiments, using reclaiming agent, the rubber combined sulfur of the reclaim did not exceed that of the parent vulcanizates. On the contrary, reductions of 0.2 to 0.3 per cent were obtained.

2. As with natural rubber, reclaiming of GR-S leads to increased zinc sulfide content. Some, though not all, of the increased sulfide sulfur arises from the reclaiming agent, a finding in line with that reported by Amberlang and Smith[3].

3. The $\frac{Q}{P}$ ratios were determined for these reclaims and they varied between 1.36 and 1.10, results of a similar order to those obtained with natural rubbers in which reclaiming agents were not used. This observation perhaps indicates that the use of the reclaiming agent does not radically change the mechanism of polymer devulcanization, or alternatively, promotes a type of degradation more akin to that which normally obtains with natural rubber vulcanizates, when reclaimed without their use.

4. It should be noted that without reclaiming agent, the vulcanizates were inadequately softened and failed to cohere on subsequent processing, while devulcanization was effective in its presence. Amberlang and Smith[3], have suggested certain reaction mechanisms for the pronounced reclaiming effects of polyalkylphenol sulfides, among which are chemical combination and consequent disruption of the sulfur crosslinks, or catalyzed oxidative scission at the sulfur links. As far as our experiments have been pursued, even very wide differences in the plasticity of the GR-S reclaims, all prepared from a standard parent vulcanizate, were not accompanied by any very significant differences in rubber combined sulfur. While recognizing that analytical determinations of such combined sulfurs give no indication of the actual mode of chemical combination, they are nevertheless difficult to reconcile with the hypothesis of crosslink disruption arising from reaction with the phenolic sulfides.

RECLAIMING OF BUTYL AND COMPARISON WITH CERTAIN TYPES OF NATURAL RUBBER RECLAIMS

This work included chemical analysis of butyl vulcanizates, both before and after reclaiming, together with a comparison of certain physical properties of vulcanized reclaims with their vulcanizates of origin. The latter was extended to commercial butyl tube scrap and natural rubber vulcanizates, one sulfurless TMT cured and the other an orthodox MBT type.

EXPERIMENTAL

	A	B	C	D	E
Natural rubber	—	—	100.0	100.0	—
Butyl rubber	100.0	100.0	—	—	10 samples of
Stearic acid	—	—	0.5	0.5	commercial butyl
Zinc oxide	5.0	5.0	6.0	6.0	tube scrap manu-
Sulfur	2.0	2.0	—	3.5	facturer's waste
TMT	1.0	1.0	3.6	—	
MBT	—	0.5	—	0.5	
SRF black	—	40.0	40.0	40.0	
Vaseline	—	0.5	0.5	0.5	

Samples A and B were cured 20 minutes at 160° C and C and D 20 minutes at 140° C.

Physicals	Optimum cure Tensile strength, psi	Elongation, %	Modulus, psi
B	2400	680	755
C	2950	570	1165
D	2465	530	850
E Average	1770	615	590

RECLAIMING

1. Each of the above were ground, reclaimed in water for 16 hours at 191° C, washed, dried, sheeted and refined.

2. A quantity of Mix A vulcanizate was ground and extracted with MEK for 48 hours, so removing uncombined sulfur, and processes as in 1.

CHEMICAL ANALYSIS

The following applies to our analyses of butyl stocks and reclaims.

(a) *Free sulfur.*—Rehner and Holowchak[4] recommended the use of methyl ethyl ketone in preference to acetone, and accordingly, 48 hours' extraction with this solvent was used throughout this work to remove uncombined sulfur.

(b) *Total sulfur.*—This was determined by a modification of the old Caspari potash-peroxide fusion method.   The rubber was very slowly fused with potash in a large covered nickel crucible, oxidized with sodium peroxide, and the sulfur estimated as $BaSO_4$.   Good reproducible results were obtained.

(c) *Sulfide sulfur.*—Kolthoff and Lignone[5], and Zapp, et al.[6], determined sulfide sulfur by first removing zinc oxide as oleate and computing sulfide sulfur from the residual zinc sulfide.   The method[7] employed here was a modification of that given in BS 903, decomposition by hydrochloric acid being preceded by 48 hours' swelling in cyclohexane.   Very consistent results were obtained by this procedure.

	Before reclaiming	After reclaiming
1. Mix A		
MEK extract	6.34	4.20
Sulfur in MEK extract	1.35	0.07
Sulfur extracted with alcholic potash	0.35	0.03
Total sulfur	2.36	1.95
Total sulfur after alcoholic potash	0.66	1.85
Sulfide sulfur	0.13	1.56
Sulfur combined to butyl rubber (as % of same)	0.59	0.32
2. Mix A after 48 hours' extraction with MEK		
Sulfide sulfur	0.13	0.43

DISCUSSION

1. As with sulfur cured natural rubber and GR-S, the reclaiming of butyl is characterized by increased sulfide sulfur.

2. Total sulfur is significantly reduced, for which no completely satisfactory explanation can be offered at this stage.

3. Our previous work has shown that the reclaiming of natural rubber vulcanizates, containing substantial amounts of acetone extractable sulfur (1–2 per cent), invariably leads to a higher rubber combined sulfur. When uncombined sulfur is substantially removed before devulcanization, for example, by open boiling in aqueous sodium sulfite or in alkali reclaiming, small reductions in rubber combined sulfur have been obtained. With butyl, even though extractable sulfur is very high at 1.35 per cent, there is a significant reduction in that combined to butyl, i.e., from 0.59 per cent to 0.32 per cent. This reduction would appear to be contained in the very large increase of sulfide sulfur from 0.13 per cent to 1.56 per cent. It is to be noted that when extractable sulfur is removed with MEK and reclaiming is carried out subsequently, there is an increase in sulfide sulfur from 0.13 per cent to 0.43 per cent. This confirms that, as a result of reclaiming, some sulfur combined to butyl in the parent vulcanizate is converted to zinc sulfide.

The water reclaiming of natural rubber, containing a significant proportion of extractable sulfur, results in both increased rubber combined sulfur and zinc sulfide. With butyl, virtually all the extractable sulfur, together with some previously combined to butyl, is converted to zinc sulfide. In this respect, butyl vulcanizates with high uncombined sulfur behave in a somewhat similar manner to natural rubber, from which this sulfur is removed before reclaiming. The following results demonstrate this point.

NATURAL RUBBER

Treatment	Free sulfur	Sulfide sulfur	Sulfur combined to rubber
Original vulcanizate	2.47	0.53	2.70
Water devulcanized 16 hr at 191° C	0.16	1.52	4.22
Free sulfur first removed with sodium sulfite and product then water devulcanized 16 hr at 191° C	0.05	0.80	2.39

BUTYL RUBBER

Treatment	Free sulfur	Sulfide sulfur	Sulfur combined to rubber
Original vulcanizate	1.35	0.13	0.59
Devulcanized in water 16 hr at 191° C	0.07	1.56	0.32

No doubt the low degree of unsaturation of butyl, as compared to natural rubber, largely accounts for the difference observed. Whereas the reaction of free sulfur with the synthetic polymer is overshadowed by reaction with zinc oxide, with natural rubber, combination with sulfur is maintained.

It is to be noted that the original butyl vulcanizates, after 48 hours' extraction with MEK, lost a further 0.35 per cent of sulfur to alcoholic potash, but there was no such loss with the reclaim. This was not reported by Zapp, et al.[6], who found that zinc sulfide formation increased with temperature and time of cure, particularly above 350° F, and that sulfide linkages were broken down to thiols. Further evidence of the breakdown of such linkages is found in the work of Farmer and Shipley[8]. Grassie[9] suggests that unsaturated polysulfides heated to 170–180° C break down to thiols and hydrogen sulfide, the latter arising from hydrogen abstraction from the α-methylene groups. Finally, Adams and Johnson[10] found that late in the vulcanization reaction, when practically all the

sulfur had reacted, the decrease in crosslinking balanced the increase in zinc sulfide so that the sum of the two remained constant. A reduction of the sulfur combined to butyl, as a consequence of reclaiming, does not appear to be out of line with presentday conceptions of the thermal stability of sulfur crosslinked vulcanizates.

EXPERIMENTAL PHYSICAL PROPERTIES BEFORE AND AFTER RECLAIMING

The resultant reclaims prepared from the Mixings B, C, D, and E, as stated, were recured and the results of the physical tests are given below.

	B	C	D	E
		Natural with carbon		
	Butyl with carbon	sulfurless cure	Natural with carbon MBT cure	Butyl tube waste
Reclaim	150.5	152.1	152.5	182.0
Stearic acid	—	2.0	2.0	—
Zinc oxide	5.0	5.0	5.0	5.0
Sulfur	2.0	3.0	3.0	2.0
TMT	1.0	—	—	1.0
MBT	0.5	0.5	0.5	0.5
DPG	—	0.2	0.2	—
Physical tests		Optimum cures		
Tensile strength	1510 psi	2500 psi	925 psi	1715 psi
Elongation	670%	430%	160%	550%
Modulus 300%	400 psi	1375 psi		730 psi

RATING

Tensile strength and elongation of reclaim as compared to those of the original scrap.

$$\text{Tensile strength} \quad \frac{1510}{2400} = 63\% \quad \frac{2500}{2950} = 84\% \quad \frac{925}{2465} = 37\% \quad \frac{1715}{1770} = 97\%$$

$$\text{Elongation} \quad \frac{670}{680} = 98\% \quad \frac{430}{570} = 75\% \quad \frac{160}{530} = 30\% \quad \frac{550}{615} = 90\%$$

$$\text{Modulus 300\%} \quad \frac{400}{755} = 53\% \quad \frac{1375}{1165} = 118\% \qquad \frac{730}{590} = 124\%$$

DISCUSSION

These results, taken in conjunction with our previous work, show that both the vulcanizing system and the polymer have a significant influence, not only on the reclaiming susceptibility, but also on the quality of the ultimate reclaim. Expressed another way, the mode of vulcanization and the nature of the polymer exert a major influence upon the resistance to degradation in water at 191° C, always assuming that degradation is measured in terms of the degree of inability of the reclaim to be revulcanized to the quality of the parent vulcanizate.

Mix B (butyl rubber reclaim) has retained some 63 per cent of its original strength and 98 per cent of its elongation, whereas with Mix E (butyl tube waste reclaim), there has been only 3 per cent loss of strength and 10 per cent loss of elongation. It is suspected that the reclaim B mix has not cured to optimum, especially since the modulus is so much lower than the original,

whereas with the tube waste E there is a 30 per cent increase in this characteristic. These results fully support the contention that butyl scrap, properly reclaimed, loses only a small fraction of its original properties and hence has such a high compounding value.

The differences between Mixes C and D are most striking. The reclaim from C was much more plastic than orthodox reclaim, whereas D was dry and "bready". The sulfurless TMT stock C retains 84 per cent of the original strength on recure, whereas MBT stock D retains only 37 per cent. While the limitations of the method of rating the various reclaims are fully recognized, the results obtained would appear to have points of interest. Both sulfur cured butyl and TMT sulfurless cured natural rubber, at least superficially, have certain common characteristics, e.g., both have very low rubber combined sulfur at their optimum cures (usually 0.4–0.6 per cent), a pronounced resistance to oxidation and an ability to replasticize readily in steam at the appropriate temperatures, i.e., they are easy to reclaim.

The plasticization of vulcanized rubber in conventional heat reclaiming processes has been stated to result mainly from oxidative scission of the hydrocarbon molecules and, while it has long been known that increasing combined sulfur, e.g., recured reclaims, prejudices replasticization, in general, crosslinkages, at least in the soft rubber range, have not been regarded as a major factor in the reclaiming mechanism. Hydroperoxidative chain scission leading to fragmentary molecules has come to be regarded as basic to devulcanization. On the other hand, it has already been proved that the chemical nature of the crosslinks themselves, e.g., sulfur or p-quinone dioxime GR-S vulcanizates, can exert a profound influence upon the efficiency of catalyzed reclaiming heat treatments[3]. Since both butyl and TMT sulfurless cures have outstanding resistance to oxidation, a reduced rate of oxidative chain scission, and hence reclaiming rate, may have been expected, but previous work, together with that here recorded, shows that these types of vulcanizates are characterized by easy plasticization and a high retention of strength in the ultimate reclaims. The latter is interpreted as being in keeping with a minimum degree of molecular chain breakdown, a condition to be anticipated from the pronounced resistance to oxidation of the original vulcanizates. While more or less hypothetical, the reclamation of butyl and TMT sulfurless stocks, from which reclaims of high quality result, could be explained on a basis of the destruction of original crosslinkages, together with a minimum of chain scission and reaggregation of fragments. The expression of fragmentary molecules, so frequently used to characterize reclaim, would appear to have less meaning where tensile strength is only relatively slightly reduced by the process of reclamation.

SUMMARY

Certain aspects of the reclamation of natural, butyl, and GR-S rubbers have been considered. While there are specific characteristic changes in all cases, e.g., zinc sulfide formation, etc., at the same time, important differences are recorded. The relation between some physical characteristics of cured reclaims and their parent vulcanizates have been discussed.

The wide differences in the quality of reclaims, dependent upon the nature of the vulcanizing system employed in the parent vulcanizate, are interpreted as being substantially in agreement with previously published work, which has demonstrated the importance of curing mechanism upon reclaiming susceptibility.

ACKNOWLEDGMENT

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SOME FACTORS WHICH DETERMINE THE FLIGHT OF SOUNDING BALLOONS

A. Angioletti and U. Felice

Unfortunately a mistake was made in Mr. Felice's name on page 1188, volume 30, of RUBBER CHEMISTRY AND TECHNOLOGY. The mistake has been corrected in the decennial index which is in the December issue of volume 30.

A STUDY OF VULCANIZATION ACCELERATORS. I. COMPOUNDS WHICH REACT ANALOGOUSLY TO RUBBER

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This paper, which appeared in RUBBER CHEMISTRY AND TECHNOLOGY, volume 30, 952 (1957), contained several errors which should be corrected as follows:

On p. 953 the left hand structural formula at the bottom of the page should not be for a ring compound at all but rather should be the formula for the isoprene unit of the natural rubber chain. Thus, the vertical C—C single bond bearing the methyl group should be changed to a double bond. The vertical single bond on the opposite side of the ring should be opened to form methylene groups of other isoprene units. On p. 955, line 24 change "hexamethylenediamine" to "hexamethylene tetramine". In line 26 change "dibenzothiazoledisulfie" to "benzothiazolyl disulfide".
On p. 958, line 15 "xylene > toluene" should be "xylene = toluene".

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